

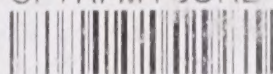
ION EXCHANGE

A LABORATORY MANUAL

SALMON AND HALE



CFTRI-MYSORE



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Ion exchange: La.



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ION EXCHANGE

A LABORATORY MANUAL

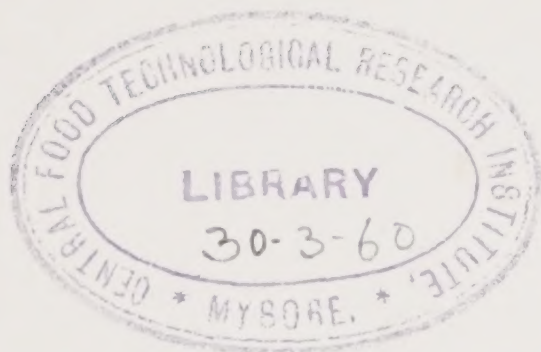
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PREFACE

THE writing of this book was prompted by many requests the authors have received to arrange practical courses in ion exchange or to give guidance on practical problems arising in the application of ion exchange. Any account of ion-exchange practice must, in our opinion, be prefaced with an account of the fundamental principles and also include details of suitable practical experiments.

We have attempted to present the principles in terms which would be understood by both sixth form pupils in schools and first year students in universities. The experiments are designed to be suitable for both school and college use and also as a possible model for research or industrial applications.

The authors wish to thank their colleagues for advice and comments; in particular they wish to acknowledge the help given by Mr C. E. A. Brownlow, who checked all the experiments, and by Mr H. Godby, who prepared the diagrams.

LONDON
February, 1959

J.E.S.
D.K.H.

CONTENTS

	PAGE
PREFACE	v
CHAPTER 1. INTRODUCTION	1
CHAPTER 2. PREPARATION OF ION-EXCHANGE RESINS	14
CHAPTER 3. PROPERTIES OF ION-EXCHANGE RESINS	31
CHAPTER 4. BEHAVIOUR OF ION-EXCHANGE COLUMNS AND ION-EXCHANGE CHROMATOGRAPHY	50
CHAPTER 5. ION-EXCHANGE TECHNIQUES AND APPAR- ATUS	65
CHAPTER 6. BASIC EXPERIMENTS WITH CATION- AND ANION-EXCHANGE RESINS	73
CHAPTER 7. SOME EXPERIMENTS IN SIMPLE COLUMN OPERATION	91
CHAPTER 8. SIMPLE ION-EXCHANGE PROCEDURES COM- MONLY EMPLOYED IN ANALYSIS	99
CHAPTER 9. APPLICATIONS OF ION EXCHANGE IN PREPARATIVE CHEMISTRY AND IN PURI- FICATION AND RECOVERY PROCESSES	109
CHAPTER 10. ION-EXCHANGE CHROMATOGRAPHY	119
CHAPTER 11. ION EXCHANGE IN THE STUDY OF COM- PLEXES	125
INDEX	133

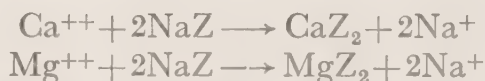
Chapter 1

INTRODUCTION

THE phenomenon of base exchange between a solid phase and a salt in solution has been known since about the middle of the nineteenth century. The first critical observations on the process appear to have been made by Thompson and Spence in 1845¹⁻³ who investigated the power of soil to absorb ammonia from ammonium sulphate. They found that if water was percolated through a glass tube containing a mixture of soil and a small quantity of ammonium sulphate, the effluent contained quite large amounts of calcium sulphate (*Figure 1*). Most of the ammonium sulphate originally added to the soil had apparently been converted into the corresponding calcium salt. The phenomenon observed by Thompson and Spence was investigated very thoroughly by Way during the period 1850-54⁴. As a result of these investigations he found that the process was not confined to the conversion of ammonium sulphate into calcium sulphate but that other salts of ammonium, sodium, potassium and magnesium could also be converted into the corresponding calcium salts. Way showed that the decomposition of an ammonium salt by the soil resulted in the production of an equivalent amount of the calcium salt; he concluded that the process was of a chemical nature and that the aluminosilicates present in the soil were responsible for the phenomenon. He also made the important discovery that aluminosilicates prepared in the laboratory from solutions of alum and sodium silicate showed very similar behaviour and that potassium nitrate, for example, could be converted into sodium nitrate by the action of a sodium aluminosilicate. Way made the interesting observation that some bases were exchanged more readily than others and that in an aluminosilicate, for example, calcium was readily replaced by ammonia but not by sodium.

INTRODUCTION

About fifty years later Gans⁵ showed that base exchange with natural and synthetic aluminosilicates could be used for water-softening on the industrial scale. In this process, the hard water containing calcium and magnesium ions is passed through a bed of a synthetic or natural zeolite. The calcium and magnesium ions in the water are replaced by sodium ions from the zeolite, and the process may be represented by the equations



in which NaZ, CaZ₂ and MgZ₂ represent the sodium, calcium, and magnesium zeolites. When the capacity of the zeolite for

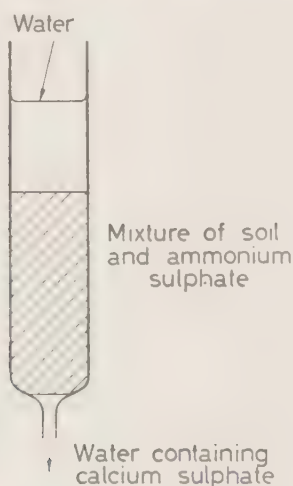
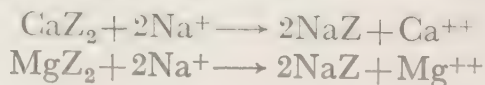


Figure 1. Early experiments of Thompson and Spence

removing calcium and magnesium ions is exhausted, the bed is treated with a concentrated solution of sodium chloride. The calcium and magnesium ions are removed from the zeolite which is converted to the sodium salt:



This process, in which the zeolite is converted back into the sodium salt, is known as 'regeneration'. After washing with water the bed can then be used again for the removal of calcium and magnesium ions.

Although the aluminosilicates were widely used in water treatment and are still employed today, they are unstable in acid and alkaline solutions and can only be used satisfactorily under nearly neutral conditions. This limitation was later overcome with the development of sulphonated coal as a base-exchange material.

A more important development took place in 1934, however, when Adams and Holmes⁶ discovered not only that certain synthetic resins could be used as base-exchange materials, i.e. for the exchange of cations, but that other resins showed anion-exchange properties. Synthetic resins which show cation-exchange properties are now known as cation-exchange resins and those which show anion-exchange properties as anion-exchange resins. By the proper use of these resins it is possible, in principle, to replace any ion in a solution by another ion of like charge by an ion-exchange process in which ions in the solution are exchanged with ions in the resin. The early cation-exchange resins prepared by Adams and Holmes were obtained by the condensation of tannins and phenol with formaldehyde; the anion-exchange resins were made by condensing aniline or metaphenylene diamine with formaldehyde. These early resins were not very stable chemically and tended to dissolve in alkaline solution. More recently, however, ion-exchange resins based on styrene polymers have been developed which have a high chemical and physical stability. The earlier ion-exchange resins were prepared in the form of granules but those based on styrene polymers are in the form of small beads with a diameter of about 1 mm or less.

Ion-exchange resins may be regarded as insoluble acids or bases which also form insoluble salts. They consist of a cross-linked polymer network to which are attached ionized or ionizable groups. The resins swell in water but the cross-links between the polymer chains prevent them from dissolving either in water or other solvents. Each particle of an ion-exchange resin can therefore be regarded as a 'giant molecule'. The functional groups can ionize into a fixed ion, which is attached to the polymer chain and is immobile, and a counter ion, or gegenion, which is mobile and can diffuse through the

INTRODUCTION

swollen resin and exchange with an ion of like charge in a surrounding solution. Cation-exchange resins contain acidic groups, e.g. $-\text{SO}_3\text{H}$, $-\text{COOH}$, or phenolic $-\text{OH}$ groups (the acidic hydrogen in these groups may of course be replaced by another cation). They can therefore be classified as strongly acidic resins or weakly acidic resins depending on the nature of the acidic group. Anion-exchange resins contain either strongly basic quaternary groups, e.g. $-\text{N}(\text{CH}_3)_3\text{OH}^-$ or weakly basic groups, e.g. $-\text{NH}_2$, $-\text{NH}\cdot\text{CH}_3$, or $-\text{N}(\text{CH}_3)_2$. The structures of a strongly acidic cation-exchange resin and a strongly basic anion-exchange resin may be represented by the diagrams shown in *Figure 2*.

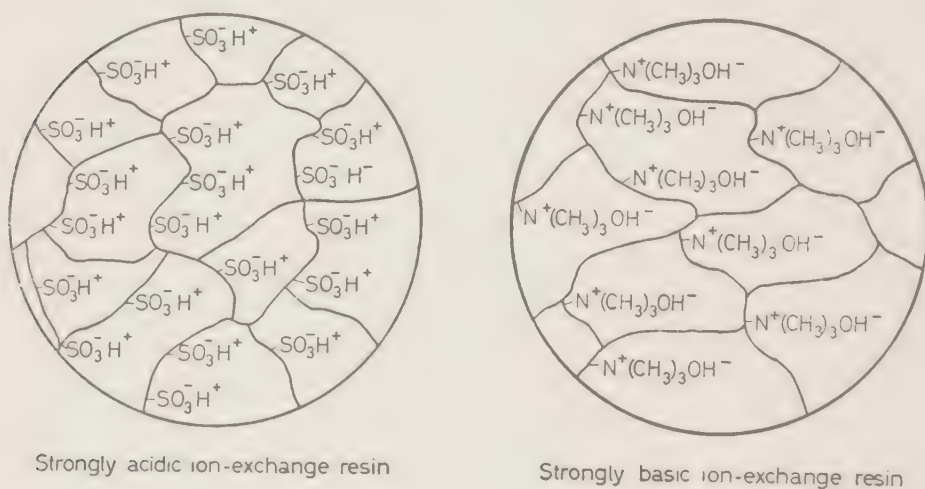
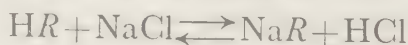


Figure 2. Structures of strongly acidic and strongly basic ion-exchange resins

The nature of the ion-exchange process can be illustrated by the reaction between a strongly acidic cation-exchange resin containing sulphonic acid ($-\text{SO}_3\text{H}$) groups and a solution of sodium chloride. The resin which contains exchangeable hydrogen ions and is said to be in the H^+ form may be denoted by HR where R represents the insoluble polymer matrix. When the resin is stirred with a solution of sodium chloride the following exchange process takes place:



Sodium ions in the solution diffuse up to the surface of the

INTRODUCTION

resin particles and through the polymer network; at the same time, an equivalent amount of hydrogen ions diffuse out into the external solution. As is shown in the above equation the reaction, which is sometimes termed 'salt-splitting', is reversible and, when equilibrium is eventually attained, a proportion of the hydrogen ions originally present in the sulphonic acid groups will have been replaced by sodium ions, and the sodium chloride in the solution will have been partially converted into hydrochloric acid. The extent of exchange will depend

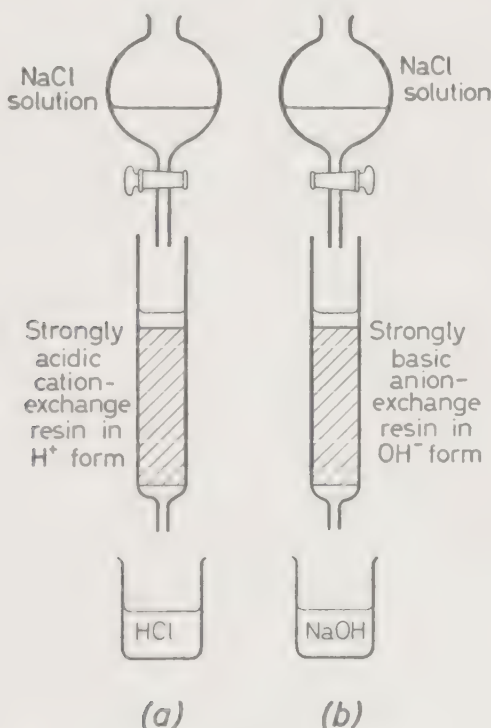


Figure 3. Column behaviour of cation- and anion-exchange resins

mainly on the affinities of the hydrogen and sodium ions for the exchange sites and the amount of sodium chloride present in the solution. If a large excess of sodium chloride is present the resin will be almost completely converted into the sodium form (NaR).

If, as shown in Figure 3(a), a solution of sodium chloride is passed through a column of a strongly acidic cation-exchange resin in the H^+ form, the hydrochloric acid formed in the

INTRODUCTION

column is removed and the exchange process will again proceed to completion. When all the hydrogen ions in the resin have been replaced by sodium ions the resin will be in the sodium form and its exchange capacity for sodium ion will be exhausted. If a solution of hydrochloric acid is now passed through the column, the sodium ions in the resin will be replaced by an equivalent amount of hydrogen ions, and the resin will be converted back into the hydrogen form.

The exchange capacity of a cation-exchange resin is usually measured in the laboratory by determining the number of milligram equivalents of sodium ion which are absorbed by one gram of the dry resin in the hydrogen form. The total exchange capacity of a strongly acidic cation-exchange resin will be determined by the concentration of the exchange sites (SO_3H groups) in the resin and, providing the exchange sites are accessible, it will be the same for all cations. The equivalent weight of the resin is the weight of resin in grams which contains one gram equivalent of exchangeable cations. If a cation-exchange resin has a total exchange capacity of 5 mg equiv./g dry resin (H form) then the equivalent weight of the resin is 200.

In the second experiment [*Figure 3(b)*] a solution of sodium chloride is passed through a column containing a strongly basic anion-exchange resin in the OH form. In this case the exchange process may be represented by the equation



The sodium chloride is converted into sodium hydroxide, and the resin is converted from the hydroxyl form into the chloride form. The resin can be changed back into the hydroxyl form by passing a solution of sodium hydroxide through the column:



The exchange capacity of an anion-exchange resin is usually determined by measuring the amount of chloride ion taken up by unit weight of the resin; the total exchange capacity will be determined by the concentration of basic groups in the resin.

INTRODUCTION

The properties of ion-exchange resins depend very greatly on the nature of the acidic or basic groups. Under acid or nearly neutral conditions, resins containing weakly acidic carboxyl groups will be largely un-ionized and they will show little or no capacity for ion exchange. Similarly, resins containing weakly basic groups will be ineffective in alkaline

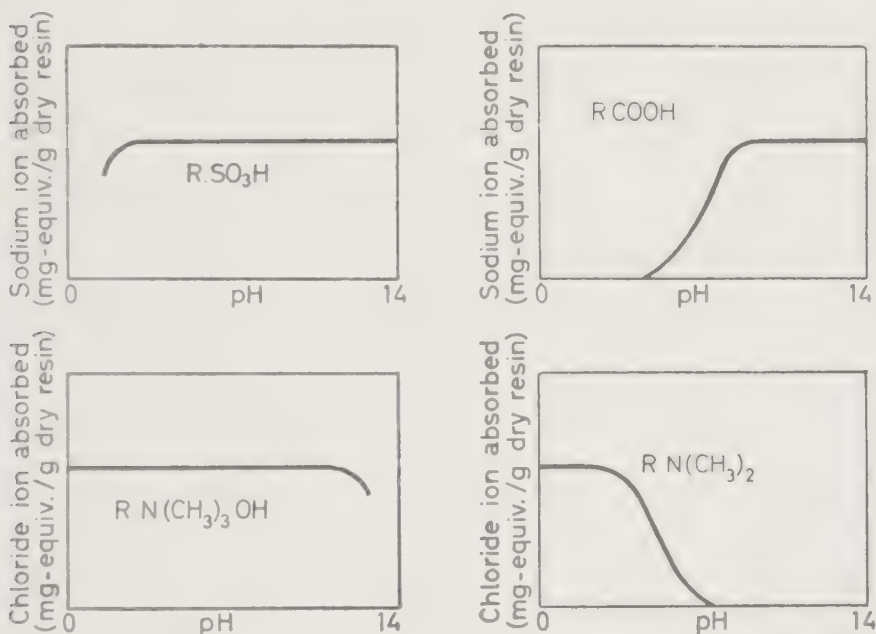


Figure 4. Titration curves of typical ion-exchange resins (in presence of 0.1 N NaCl)

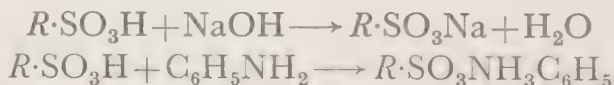
solutions. Strongly acidic and strongly basic resins, however, are effective over a very wide pH range and can be used under acid, neutral and alkaline conditions. Information on the nature and concentration of the acidic or basic groups in an ion-exchange resin can be obtained from 'titration curves'. In the case of a cation-exchange resin, the titration curve is usually obtained by measuring the amount of sodium ion which is taken up by the hydrogen form of the resin when it is in equilibrium with sodium chloride solutions (usually 0.1 N or 1 N) of differing pH. The titration curve of an anion-exchange resin is usually obtained by measuring the capacity of the free base form of the resin for chloride ion under different

pH conditions. Typical titration curves of unfunctional ion-exchange resins (i.e. resins containing only one type of functional group) are shown in *Figure 4*. The exchange capacity of the weakly acidic and basic resins depends markedly on the pH of the solution but the capacity of the strongly acidic and strongly basic resins is very largely independent of the pH of the solution. The maximum exchange capacity on the titration curve corresponds to the total exchange capacity of the resin.

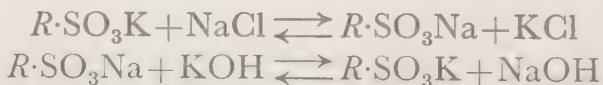
The differences in the behaviour of the different types of ion-exchange resins can be illustrated by some typical reactions.

(1) Strongly acidic resins (containing $\text{—SO}_3\text{H}$ groups)

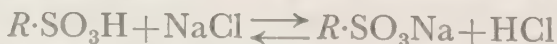
(a) *Neutralization of bases*—Strongly acidic resins in the hydrogen form can be used for the neutralization or absorption of bases. If an excess of resin is present the base will be completely absorbed, e.g.



(b) *Base exchange*—Strongly acidic resins can be used for base-exchange reactions in neutral or alkaline solutions, e.g.



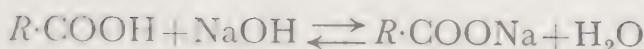
(c) *Salt-splitting*—A characteristic property of strongly acidic resins is their ability to 'split' the salts of strong acids



This process is normally the first stage when ion-exchange resins are used for the removal of salts from water or aqueous solutions of non-electrolytes. In the reverse process an excess of strong acid is required to regenerate the acid form of the resin from its salt.

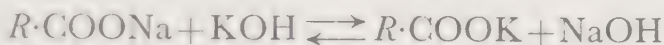
(2) Weakly acidic resins (e.g. containing —COOH groups)

(a) *Neutralization of bases*—Weakly acidic resins will absorb strong bases but as the salt form of the resin hydrolyzes, the base may not be completely absorbed even if an excess of resin is present



Weak bases are not usually absorbed to any appreciable extent.

(b) *Base exchange*—Since their salts hydrolyze, weakly acidic resins can only be used for base-exchange reactions in alkaline solutions, e.g.



(c) *Salt-splitting*—Little or no exchange occurs with weakly acidic resins in the hydrogen form and solutions containing the salts of strong acids



As indicated in the above equation the reverse reaction does, however, take place very readily.

(3) Strongly basic resins [e.g. containing $-\text{N}(\text{CH}_3)_3\text{OH}$ groups]

(a) *Neutralization of acids*—Strongly basic resins in the hydroxyl form can be used for the absorption of both strong and weak acids



Since strongly basic resins will absorb very weak acids they are used in water treatment for the removal of carbon dioxide and silica. An excess of strong base is required for the regeneration of strongly basic resins.

(b) *Acid exchange*—Strongly basic resins can be used over a wide pH range for the exchange of anions, e.g.



(c) *Salt-splitting*—Like the strongly acidic cation-exchange resins, the strongly basic resins are capable of splitting the salts of strong acids, e.g.



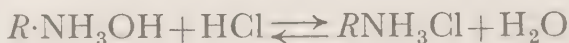
(4) Weakly basic resins (e.g. containing $-\text{NH}_2$ groups).

INTRODUCTION

(a) *Neutralization of acids*—Weakly basic resins can be used for the absorption of strong acids, e.g.

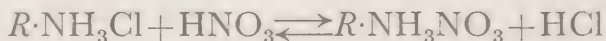


Since this process can be regarded as ion-exchange rather than acid absorption it is sometimes represented by the equation



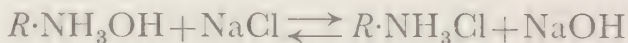
As shown in the equation, the salt form of the resin is readily hydrolyzed by water. Weak acids such as carbon dioxide are only absorbed to a slight extent by weakly basic resins but these resins are used in water treatment when complete removal of carbon dioxide is unnecessary.

(b) *Acid exchange*—Weakly basic resins can be used satisfactorily in acid solutions for the exchange of anions, e.g.



but cannot generally be used for the exchange of anions in neutral or alkaline solution.

(c) *Salt-splitting*—As with the weakly acidic resins, little exchange occurs with weakly basic resins and solutions of the salts of strong acids, but basic resins in the salt form are readily regenerated with alkali



Important differences in the rates of exchange are observed with the different types of ion-exchange resin. With the strongly acidic and strongly basic resins equilibrium is normally attained in a matter of minutes or even seconds; with a weakly acidic resin in the hydrogen form or a weakly basic resin in the hydroxyl form several hours may be required. When these resins are in the salt form, however, the rate of reaction is usually rapid.

The characteristic properties of the four different types of ion-exchange resin are summarized in *Table 1*. Since they can be used over a wide pH range and show high rates of exchange, strongly acidic and strongly basic resins are used

Table 1. Characteristics of typical ion-exchange resins

	Cation-exchange resins		Anion-exchange resins	
	Strongly acidic	Weakly acidic	Strongly basic	Weakly basic
Functional group	Sulphonic	Carboxylic	Quaternary ammonium	Amino
Effect of pH on exchange capacity	Capacity largely independent of pH	Negligible capacity in acid solutions	Capacity largely independent of pH	Negligible capacity in alkaline solutions
Salts	Stable	Hydrolyze on washing	Stable	Hydrolyze on washing
Regeneration	Excess of strong acid required	Readily regenerated	Excess of strong base required	Readily regenerated with sodium carbonate or ammonia
Rates of exchange	Rapid	Slow unless ionized (i.e. in alkaline medium)	Rapid	Slow unless ionized (i.e. in acid medium)

INTRODUCTION

most frequently in the laboratory. In special cases, however, weakly acidic and weakly basic resins are employed.

Most of the laboratory applications of ion-exchange resins can be divided into three groups:

- (1) Simple exchange applications in which ions in the solution are replaced by ions from the resin.
- (2) Separations by ion-exchange chromatography.
- (3) Catalysis.

The simple exchange applications include the preparation of acids, bases and salts, and the removal of salts from water and aqueous solutions. In the de-ionization of solutions the cations are replaced by hydrogen ions and the anions by hydroxyl ions; the salts are therefore replaced by an equivalent amount of water. Many of the simple exchange procedures can be adapted for analytical purposes; salts can be determined by titration with alkali or acid after they have been converted to the corresponding acids or bases, and ions which interfere in other analytical procedures can be removed by de-ionization or replaced by non-interfering ions. Since ions which have been absorbed by a resin can often be removed in a more concentrated solution, ion-exchange resins can be used for the concentration of ions from dilute solutions. In the laboratory, the study of the distribution of ions between an ion-exchange resin and a solution has proved of great importance in the investigation of inorganic complexes.

If an ion-exchange resin is in equilibrium with a solution containing a mixture of ions, the extent to which the different ions are absorbed will depend on the concentrations of the ions and their affinities for the resin. Ion-exchange resins can therefore be used for the separation of mixtures of ions of like charge and, if a chromatographic procedure is employed, complex mixtures of closely related ions, e.g. those of the rare earth metals, can be completely separated.

Since ion-exchange resins are essentially insoluble acids or bases they can be used as catalysts in organic reactions catalyzed by acids or bases. If an ion-exchange resin is employed as a catalyst it can be readily removed from the reaction mixture and the products of the reaction are easily isolated.

INTRODUCTION

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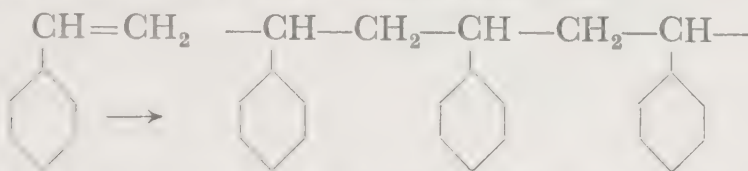
Chapter 2

PREPARATION OF ION-EXCHANGE RESINS

THE earlier ion-exchange resins were made by methods similar to those used by Adams and Holmes. Cation-exchange resins were obtained, for example, by the condensation of a phenol or phenol-sulphonic acid with formaldehyde, and anion-exchange resins by the condensation of amines with formaldehyde. These earlier resins, however, have been largely superseded by ion-exchange resins based on cross-linked polystyrene, which have greater chemical and physical stability. The first ion-exchange resin of this type was obtained by the sulphonation of cross-linked polystyrene; this method of synthesis which was originally described by D'Alelio¹ gives a cation-exchange resin with a high exchange capacity and of exceptional stability. A few years later, methods were developed for the introduction of quaternary ammonium groups into cross-linked polystyrene, and strongly basic resins became commercially available. Methods have also been devised for the introduction of weakly acidic and weakly basic groups into cross-linked polystyrene so that resins of the four main types can be obtained from this important intermediate. Since resins based on cross-linked polystyrene are now generally employed in the laboratory and since their properties depend in part on the structure of the cross-linked polystyrene, a knowledge of the methods used in the preparation of this intermediate is of considerable help in understanding the behaviour of the acidic and basic resins. The methods used for the preparation of cross-linked polystyrene and the more important ion-exchange resins are described in the following paragraphs. The preparation of chelating resins, ion-exchange papers and some other special ion-exchange materials are described in the final subsections of this chapter.

Cross-linked Polystyrene

Styrene will polymerize under a variety of conditions to give polystyrene, a linear polymer of high molecular weight which is soluble in aromatic and chlorinated solvents



The styrene monomer can be polymerized alone (mass polymerization), in solution, or as an emulsion or suspension in water. In all cases the rate of polymerization increases very rapidly with rise in temperature, and can also be increased by the use of catalysts.

For the preparation of ion-exchange resins, a copolymer of styrene and divinylbenzene is usually employed. If styrene, containing a small proportion of divinylbenzene, is allowed to polymerize, a three dimensional polymer network is formed in which polystyrene chains are linked together at intervals by divinylbenzene units which have been incorporated in two polymer chains (*Figure 5*). The copolymer obtained will not melt and is insoluble in all solvents; it will swell in organic solvents, such as benzene or toluene, but not in water or aqueous solutions. Each particle of a cross-linked polystyrene resin can be regarded as a 'giant molecule' in which cross-linked polymer chains extend through the particle in all directions.

In the preparation of ion-exchange resins, the cross-linked polystyrene is invariably prepared by suspension polymerization; the mixture of monomers is dispersed as small droplets in an aqueous solution and the copolymer is then obtained in the form of small beads 1 mm or less in diameter. These beads are physically stable, very convenient to handle, and the waste involved in the disintegration of resins prepared in massive form is avoided, since a product with a predetermined particle size range can readily be obtained. Suspension polymerization is essentially similar to mass polymerization and so monomer soluble catalysts are more effective than the water soluble catalysts employed in emulsion polymerization.

INTRODUCTION

However, since the monomers are dispersed into discrete globules in an aqueous solution the polymerization temperature is more easily controlled than in mass polymerization. To prevent aggregation of the monomer droplets during the course of the polymerization, a suspension stabilizer, such as polyvinyl alcohol, bentonite, starch, or an alginate must be used. In the laboratory, starch or 'Promulsin' (a cellulosic

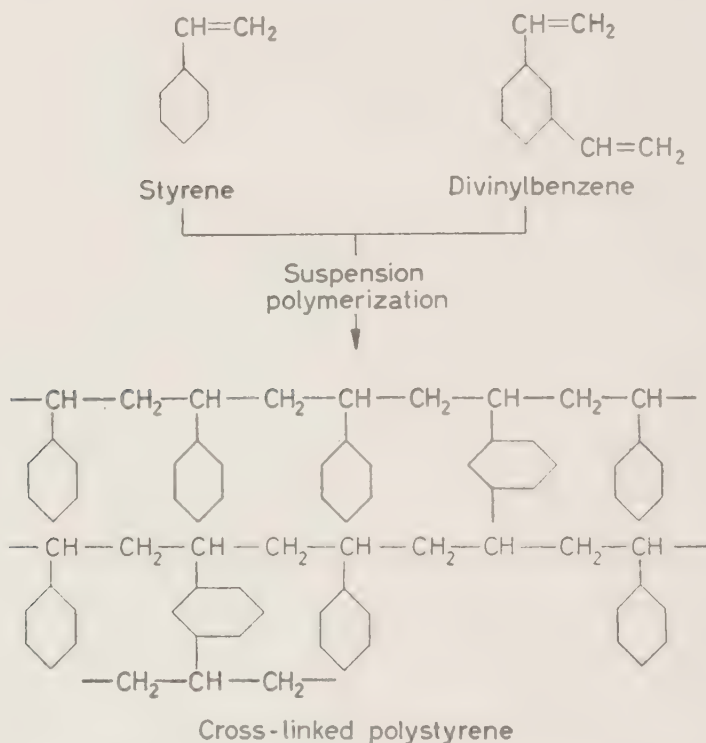


Figure 5. Preparation of cross-linked polystyrene

derivative) have been employed; the latter has proved to be particularly convenient since the mixture of monomers and catalyst can be dispersed in a solution of the 'Promulsin' by vigorous shaking until droplets of the required size have been obtained. The suspension is very stable and further shaking or stirring during the polymerization is not required. The mean particle size and the particle size distribution of the copolymer are determined mainly by the degree of mechanical agitation employed in the preparation of the suspension, the

viscosity of the solution, and the nature of the suspension stabilizer. For the preparation of ion-exchange resins, beads of the copolymer with a mean particle diameter in the range 50–1,000 microns are usually required. The proportion of divinylbenzene may be varied over a wide range: for the commercial resins used in water treatment, 8–12 per cent divinylbenzene is generally used but resins containing 1–20 per cent divinylbenzene are available for laboratory use. Pure divinylbenzene (DVB) is difficult to prepare and a commercial solution, consisting of divinylbenzene isomers in ethylstyrene with a little saturated material, is normally used. For the polymerization of the styrene and divinylbenzene a monomer

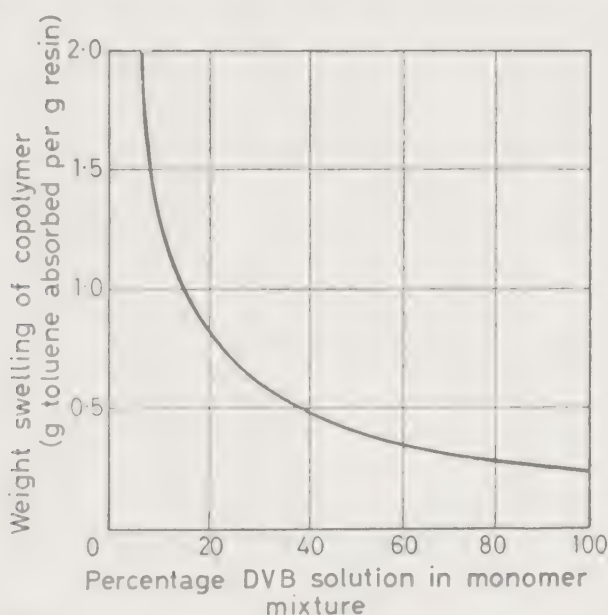


Figure 6. Swelling of cross-linked polystyrenes in toluene

soluble catalyst, e.g. benzoyl peroxide, is used and the polymerization is carried out at an elevated temperature. For the preparation of cross-linked polystyrene in the laboratory the following procedure has been described²:

47 ml Styrene, 3 ml DVB solution (*ca.* 33 per cent DVB) and 0.5 g benzoyl peroxide were added to a beer bottle containing 450 ml of a 2 per cent aqueous solution of 'Promulsin'. The monomers were dispersed in the aqueous medium by shaking

INTRODUCTION

the beer bottle for 5 min in a reciprocating laboratory shaker at room temperature. The beer bottle was then immersed overnight in a water bath maintained at 80°C. The product was boiled with 2 N sulphuric acid to hydrolyze the 'Promulsin', washed thoroughly on a filter, dried at 50°C and sieved.

If suitable conditions are used, very little aggregation occurs and the product is almost entirely in the form of small spherical beads.

The extent to which the cross-linked polystyrene will swell in a solvent, such as benzene or toluene, is determined by the degree of cross-linking. Copolymers containing a high proportion of divinylbenzene will absorb from 0.25 to 0.50 g toluene per g resin. If the proportion of divinylbenzene is decreased, however, the weight swelling in toluene increases very rapidly (*Figure 6*).

Strongly Acidic Cation-exchange Resins

The most important strongly acidic cation-exchange resins are prepared by the sulphonation of cross-linked polystyrene (*Figure 7*). Various sulphonating agents, e.g. fuming sulphuric acid, chlorosulphonic acid, sulphur trioxide in nitrobenzene, or concentrated sulphuric acid, can be used. In the laboratory, sulphuric acid has proved to be very suitable and a typical procedure is that described by Pepper²:

1,500 ml concentrated sulphuric acid with 2 g silver sulphate were heated in a three-necked flask to 80–90°C with stirring. 200 g cross-linked polystyrene beads (50–250 μ diameter, 5 per cent nominal DVB content) were then added. Owing to an exothermic reaction, the temperature rose to 100°C, at which the reactants were maintained for 6 h. After cooling overnight, the product was poured into 50 per cent sulphuric acid, which was cooled and diluted slowly with distilled water. The resin was thoroughly washed on a filter, transferred to a column and treated alternately with 2 N NaCl and 2 N HCl. After the final treatment with acid, the resin was washed exhaustively in the column.

The proportions of sulphuric acid and cross-linked polystyrene are not critical but the mixture is stirred more easily if at least a fivefold excess of acid is used. The degree of

sulphonation of the cross-linked polystyrene can be determined by measuring the total exchange capacity. A known volume of standard sodium hydroxide solution is added to a sample of the resin in the hydrogen form, and when equilibrium is attained, the excess sodium hydroxide is determined by titrating an aliquot of the solution with standard acid. The total exchange capacity of the resin can then be calculated from the amount of sodium hydroxide neutralized by the resin and the dry weight of the sample.

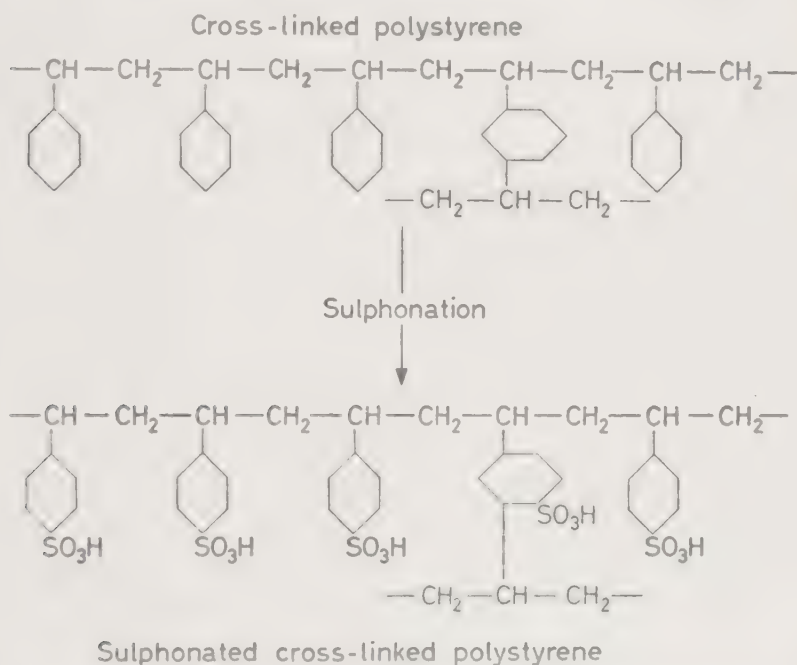


Figure 7. Preparation of a strongly acidic cation-exchange resin

The rate of sulphonation depends on the particle size of the copolymer beads but, if sufficient time is allowed, a well-defined limiting exchange capacity is attained and no further increase in capacity is observed when the cross-linked polystyrene is heated for a longer time in the sulphuric acid (*Figure 8*). Material with a broad particle size distribution can therefore be sulphonated uniformly if sufficient time is allowed for the complete sulphonation of the large particles.

The rate of sulphonation also depends on the degree of cross-linking of the copolymer and long sulphonation times may be required with highly cross-linked resins. If the copolymer

INTRODUCTION

beads are first allowed to swell in a solvent such as toluene, nitrobenzene or methylene chloride, however, the rate of sulphonation is increased, and beads which are free from cracks are more easily obtained.

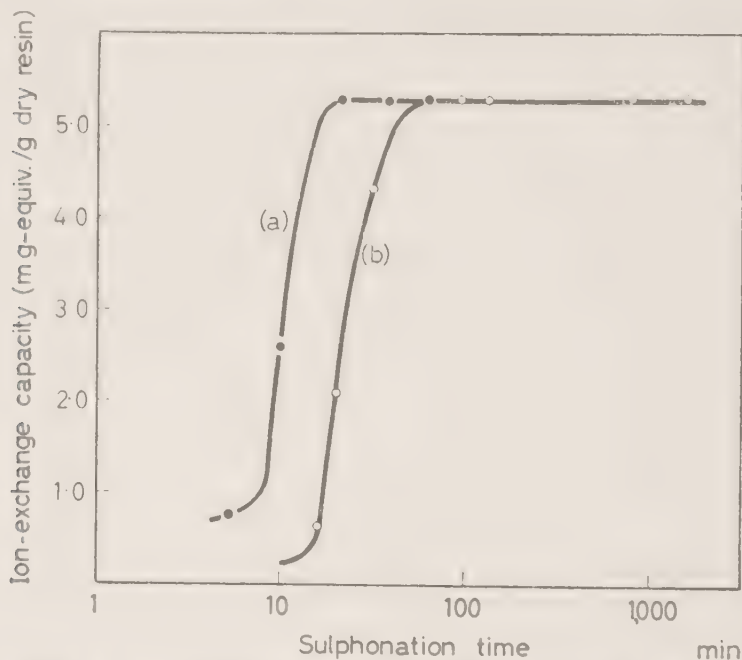


Figure 8. Sulphonation of cross-linked polystyrene (5 per cent DVB) with sulphuric acid at 100°C: (a) particle diameter: 30–50 μ ; (b) particle diameter: 100–150 μ (From K. W. Pepper², by courtesy of Journal of Applied Chemistry)

It has been found that, when sulphuric acid is used as the sulphonating agent, the limiting exchange capacity corresponds to the introduction of one sulphonic acid group into each benzene nucleus; the sulphur contents and exchange capacities are in good agreement with calculated values and the resins are therefore essentially monofunctional. Values obtained for the exchange capacity are compared in Table 2 with theoretical values calculated by assuming that the DVB solution consists of divinylbenzene and ethylstyrene, that the three monomers copolymerize uniformly, and that one sulphonic acid group is introduced into each benzene ring in the copolymer.

The sulphonated polystyrene resins are very stable, both

physically and chemically; they can be used at temperatures up to 120°C and are resistant to concentrated acids and alkalis and most oxidizing and reducing agents.

Table 2. Observed and theoretical ion-exchange capacities of sulphonated cross-linked polystyrene resins²

<i>Nominal divinylbenzene content %</i>	<i>Ion-exchange capacity (mg-equiv./g dry resin)</i>	
	<i>Observed</i>	<i>Theoretical</i>
2	5.35	5.39
5	5.30	5.34
10	5.25	5.24
17	5.05	5.11
33	4.55	4.74

Weakly Acidic Cation-exchange Resins

The earlier weakly acidic resins containing carboxylic acid groups were prepared by polycondensation reactions, for example, by the condensation of 1:3:5 resorcylic acid with formaldehyde. These resins are somewhat unstable, however, and carboxylic resins based on vinyl polymers are now usually employed. Carboxylic acid groups can be introduced into cross-linked polystyrene³ but methods of the type shown in *Figure 9* in which methacrylic acid is copolymerized with divinylbenzene are now generally used. Resins prepared from a mixture of methacrylic acid and 5–10 per cent divinylbenzene with 1 per cent benzoyl peroxide as catalyst have a suitable swelling in water for most applications⁴. Cation-exchange resins of this type have an exceptionally high capacity (approx. 10 mg-equiv./g dry resin).

Strongly Basic Anion-exchange Resins

The earlier anion-exchange resins were based on polycondensation reactions and, although methods for the introduction of quaternary ammonium groups had been devised previously, it was not until 1948 that strongly basic resins derived from

INTRODUCTION

cross-linked polystyrene became available. Various procedures for the introduction of quaternary ammonium groups into a cross-linked polystyrene matrix have been described but most methods are similar to that shown in *Figure 10*⁵. The cross-linked polystyrene is first treated with chloromethyl

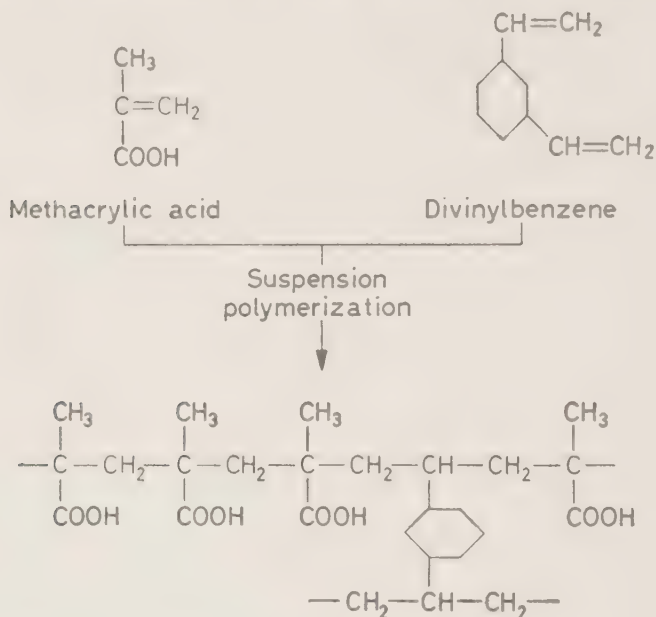


Figure 9. Preparation of a weakly acidic cation-exchange resin

methyl ether in the presence of a catalyst such as aluminium chloride, zinc chloride or stannic chloride. The chloromethylated product is then allowed to react with a tertiary amine such as trimethylamine or dimethylethanolamine. If trimethylamine is employed (as in *Figure 10*) a strongly basic anion-exchange resin of Type I is obtained; if dimethylethanolamine is used, the resin is less strongly basic and is usually described as a Type II resin. A procedure which has been employed in the laboratory for the preparation of strongly basic anion-exchange resins is described below⁶:

In a typical experiment under reflux, the ether (200 ml.) was added to copolymer beads (50 g), which were allowed to swell at room temperature for 1 h and then warmed while being stirred. On addition of 100 ml. of the ether containing 15.2 g of stannic chloride, the mixture boiled, and it was kept at reflux

PREPARATION OF ION-EXCHANGE RESINS

temperature for 1 h. The product was cooled, filtered off, and washed with aqueous dioxan. In order to remove residual catalyst, the product was transferred to a column and washed slowly with aqueous dioxan containing 10 per cent (*v/v*) of concentrated hydrochloric acid and finally with dioxan alone.

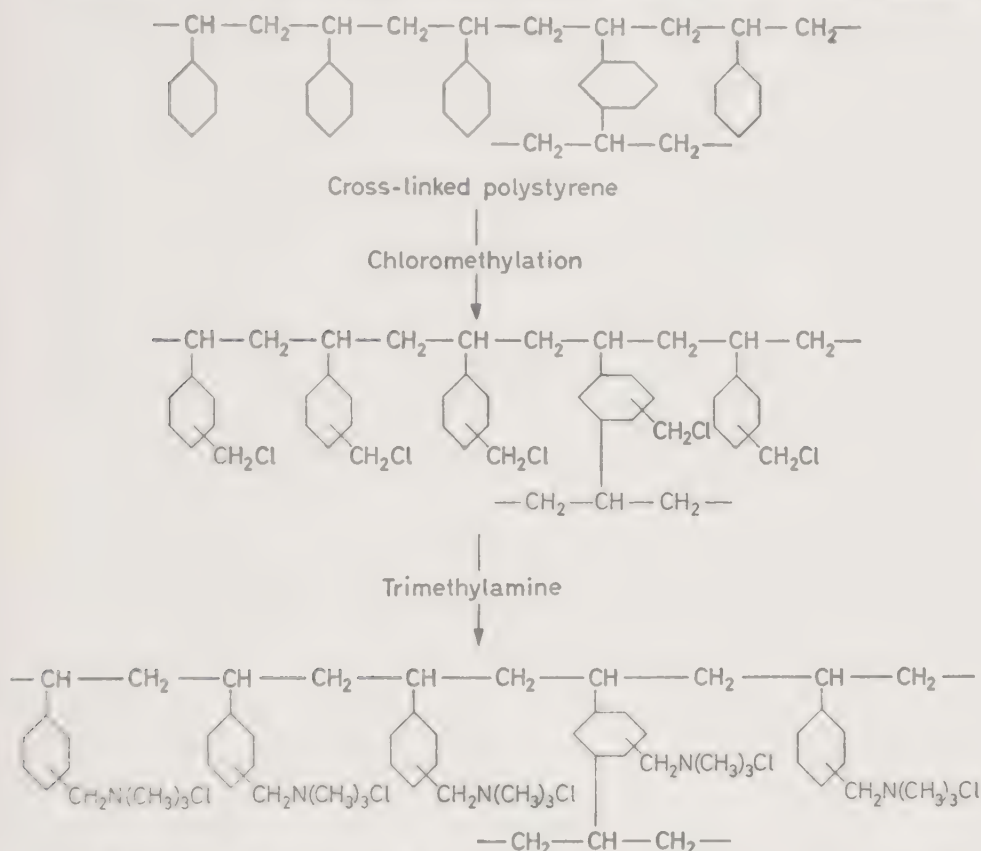


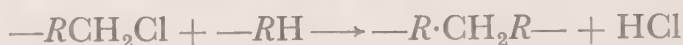
Figure 10. Preparation of a strongly basic anion-exchange resin

Anhydrous trimethylamine was used for the preparation of the strongly basic resins. 20 g of chloromethylated copolymer (2 per cent of divinylbenzene) were swollen in dioxan and cooled to 0°C. 100 ml. of the amine at 0°C were added and, after slight warming to dissolve the amine, the mixture was kept at 0°C for two days with intermittent shaking (7½ per cent divinylbenzene copolymers require seven days at 0°C). After filtration, the product was washed in a column with 2 N hydrochloric acid for 2–3 days, and then treated alternately with 0.1 N sodium hydroxide and 2 N hydrochloric acid, three times. The acid and alkali solutions were passed through guard tubes, containing strongly basic resin in the chloride or the hydroxyl form, respectively. Finally,

INTRODUCTION

the resin was treated with 2 M sodium chloride solution and washed with de-ionized water, until the effluent was chloride-free. The de-ionized water was passed through a small mixed bed of strongly acidic and strongly basic resins, immediately above the column; in this way, absorption of carbonate ion by the sample was avoided.

The exchange capacity of the resin obtained depends ultimately, of course, on the extent of chloromethylation during the first reaction. Unfortunately, the chloromethylation of cross-linked polystyrene is not so easily controlled as the sulphonation reaction, and it has been shown that a secondary reaction takes place between a chloromethyl group attached to one benzene ring and another aromatic nucleus,



As a result, methylene bridges are formed between neighbouring aromatic nuclei and, if these are in different polymer chains, additional cross-linkages will be introduced into the polymer network. For the preparation of commercial strongly basic anion-exchange resins, cross-linked polystyrene containing about 6–8 per cent divinylbenzene is commonly employed, but resins containing from 1 to 10 per cent divinylbenzene are available for laboratory use. However, since additional cross-links may be introduced during the preparation of these resins, the weight swelling in water (or the 'water regain') may be a more reliable guide to the degree of cross-linking of the final resin.

The exchange capacity of commercial strongly basic anion-exchange resins based on cross-linked polystyrene is usually about 3.5–4 mg-equiv./g dry resin. Resins of both types are stable in the salt form up to about 50°C and in the free base form possess good stability at room temperature. Strongly basic resins of Type I have been found to be more stable than Type II and are thus used more frequently in the laboratory.

Weakly Basic Anion-exchange Resins

If aniline or *m*-phenylene diamine is condensed with formaldehyde, a weakly basic anion-exchange resin is obtained. This method of preparation was used by Adams and Holmes

PREPARATION OF ION-EXCHANGE RESINS

and similar condensation reactions were used for the preparation of the earlier commercial anion-exchange resins. Weakly basic anion-exchange resins of greater stability which are based on cross-linked polystyrene are now available, however, and are obtained by treating chloromethylated cross-linked polystyrene with ammonia, or primary or secondary amines (Figure 11). With a secondary amine, such as dimethylamine or diethylamine, a monofunctional resin containing tertiary amine groups can be obtained in the laboratory but resins produced industrially may contain a considerable proportion of quaternary groups. These resins are therefore often described as mixed base resins. With ammonia or primary amines, polyfunctional resins containing primary, secondary and tertiary amine groups are obtained and additional cross-linking may be introduced during amination.

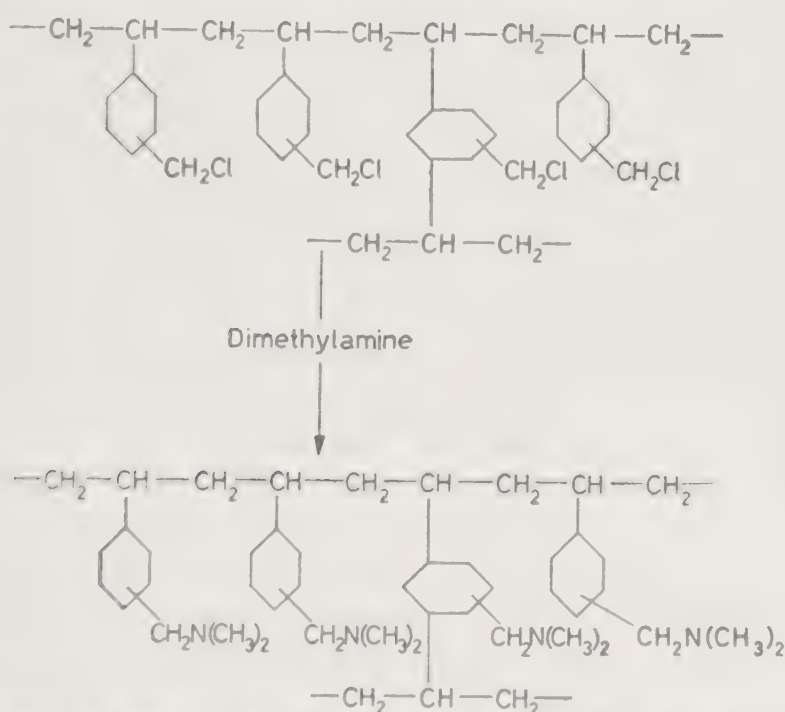


Figure 11. Preparation of weakly basic anion-exchange resins

The total exchange capacity of weakly basic anion-exchange resins based on cross-linked polystyrene depends on the nature of the amine used in the preparation. If a secondary amine, such as diethylamine, is used a monofunctional resin with a

total exchange capacity of about 3–3.5 mg-equiv./g dry resin is obtained; polyfunctional resins with exchange capacities up to 5 or 6 mg-equiv./g dry resin can be made by using polyethylene polyamines such as tetraethylenepentamine. The weakly basic resins based on cross-linked polystyrene have a high thermal stability and can be used in both the salt and free base forms at temperatures up to 100°C.

Chelating Resins and Other Special Ion-exchange Materials

For a long time there has been considerable interest in the synthesis of ion-exchange resins containing special functional groups. These groups might, for example, be chelating groups, in which case the resin might be expected to absorb certain metal ions selectively, or they might be optically active groups, in which case the resin might be used for the separation of optically active isomers. The first attempt to prepare a chelating resin was made about 1940 by Skogseid who synthesized a polystyrene resin containing groups similar in structure to dipicrylamine. Since dipicrylamine forms a sparingly soluble potassium salt, Skogseid expected the resin to absorb potassium selectively and he was, in fact, able to show that this resin did absorb potassium rather more strongly than other cation-exchange resins. Since the work of Skogseid other chelating resins have been described^{7,8}, but with most of these resins the rates of exchange are slow and they have found little practical application.

In many laboratory applications, and particularly in qualitative analysis, an ion-exchange material in the form of a paper would have advantages over materials in the form of small particles which must be packed into columns. Ion-exchange properties can be conferred on filter paper by the introduction of acidic or basic groups into the cellulose molecule^{9,10}, and ion-exchange papers can be prepared from aminated or phosphorylated cellulose¹¹. In other methods for making ion-exchange papers, a finely divided ion-exchange resin is incorporated in the pulp which is used for the preparation of the paper¹², or filter paper is passed through a suspension of the finely divided resin¹³.

PREPARATION OF ION-EXCHANGE RESINS

Although many other special ion-exchange materials have been described, many of these are only of ephemeral interest, but some are likely to be of importance in special applications. For example cation- and anion-exchange resins have been converted into specific adsorbents for proteins. A specific antigen is combined with the resin either by chemical reaction or physical adsorption; the resin-antigen complex can then be used for the adsorption of the specific antibody¹⁴.

Table 3. Equivalent ion-exchange resins

	<i>The Permutit Co. Ltd., London</i>	<i>Chemical Process Co., U.S.A.</i>	<i>Dow Chemical Co., U.S.A.</i>	<i>Rohm and Haas Co., U.S.A.</i>	<i>Farbenfabriken Bayer, Leverkusen</i>	<i>VEB Farbenfabriken, Wolfen</i>
<i>Cation-exchange resins</i>	<i>Zeo-Karb</i>	<i>Duolite</i>	<i>Dowex</i>	<i>Amberlite</i>	<i>Lewatit</i>	<i>Wofatit</i>
Sulphonated phenolic resins	215	—	30†	IR-1†	KS, KSB† KSN	KS†
	315†	C-3 C-10 C-20*	—	IR-100† IR-105*† IR-120*	PN	P
Sulphonated polystyrene resins	225*	—	50* 50W	—	S-100*	KPS-200*
	¶	C-21*†† C-25*†† C-26*††	¶	IR-112*††	—	—
	¶	—	¶	IR-122*§ IR-124*§	—	—
Carboxylic resins	216	CS-100	—	—	C,CN CNO	C,CN
	226*	CS-101*	—	IRC-50*	—	CP-300
<i>Anion-exchange resins</i>	<i>De-Acidite</i>	<i>Duolite</i>	<i>Dowex</i>	<i>Amberlite</i>	<i>Lewatit</i>	<i>Wofatit</i>
Strongly basic anion-exchange resins (Type I)	FF*	A-42*	1*	IRA-400*	MII (or MN)	L
	¶	A-101*†	¶ 21K†	IRA-401*†† IRA-402*††	—	—
Strongly basic anion-exchange resins (Type II)	—	A-40*	2*	IRA-410*	—	—
	—	A-102*†	¶	IRA-411*††	—	—
Weakly basic anion-exchange resins	B†	A-2, A-4	—	IR-4B	MI	M,N
	E	A-5, A-6, A-7 A-10, A-70	—	—	MIH	MD
	G* H*** J*	A-14*	3*	IR-45*	—	—
	—	A-114*†	—	—	—	—

* Bead resin

† Manufacture discontinued

‡ Porous resin

§ Highly cross-linked resin

|| Light amber to white in colour

¶ Resins of different degrees of cross-linking are available from the manufacturers

*** Mixed base resin

The table shows resins which are equivalent in type; they may not be exactly equivalent in performance

The absence of a resin from this table does not mean that it is not available from the manufacturers

INTRODUCTION

Table 4. Special ion-exchange resins for laboratory use

'Permutit' Chromatographic Resins

Manufactured by The Permutit Co. Ltd., London, W.4. Available from (1) The Permutit Co. Ltd.; (2) The British Drug Houses, Ltd., Poole, Dorset; (3) Hopkin and Williams, Ltd., Chadwell Heath, Essex.

Zeo-Karb 225 (SRC 1-24) Polystyrene sulphonic acid resin, sodium form, capacity 4.5-5.0 mg eq./g

Cross-linking	1	2	4.5	8	12	20%
Water regain	6-12	3-5	1.5-2	0.9-1.1	0.6-0.9	0.4-0.6

Zeo-Karb 226 (SRC 41-48) Polymethacrylic acid, hydrogen form, capacity 9-10 mg eq./g

Cross-linking	2½	4½%
Water regain	0.8-1.0	0.6-0.8

De-Acidite FF (SRA) 61-72) Strong base polystyrene quaternary ammonium resins, chloride form, capacity 4.0 mg eq./g

Cross-linking	approx	2-3	3-5	7-9%
Water regain		1.5-2.0	1.0-1.5	0.6-1.0

De-Acidite G (SRA) 91-102) Weak base polystyrene tertiary amine resin, hydrochloride form, capacity 4.0 mg eq./g

Cross-linking	approx	2-3	3-5	7-9%
Water regain		1.5-2.0	1.0-1.5	0.6-1.0

De-Acidite H (SRA 121-132) Mixed base polystyrene tertiary and quaternary resin, chloride-hydrochloride form, capacity 3.8 mg eq./g

Cross-linking	approx	2-3	3-5	7-9%
Water regain		1.5-2.0	1.0-1.5	0.6-1.0

The above resins are available in the following wet particle size ranges: 14-52, 52-100, 100-200 and <200 BSS Mesh

'Amberlite' Chromatographic Grade Ion-exchange Resins

Manufactured by the Rohm and Haas Company, Philadelphia. Available in the U.K. from The British Drug Houses, Ltd., Poole, Dorset.

<i>Designation</i>	<i>Type</i>	<i>Dry particle size range (U.S. standard screens)</i>
<i>Amberlite IR-120</i>		
CG-120 Type I	Strongly acidic cation exchanger	100-200 mesh
CG-120 Type II	Strongly acidic cation exchanger	200-400 mesh
CG-120 Type III	Strongly acidic cation exchanger	400-600 mesh
<i>Amberlite IRA-400</i>		
CG-400 Type I	Strongly basic anion exchanger	100-200 mesh
CG-400 Type II	Strongly basic anion exchanger	200-400 mesh

PREPARATION OF ION-EXCHANGE RESINS

Table 4—continued

Amberlite IRC-50

CG-50 Type I	Weakly acidic cation exchanger	100-200 mesh
CG-50 Type II	Weakly acidic cation exchanger	200-400 mesh
CG-50 Type III	Weakly acidic cation exchanger	400-600 mesh

Amberlite IR-45

CG-45 Type I	Weakly basic anion exchanger	100-200 mesh
CG-45 Type II	Weakly basic anion exchanger	200-400 mesh

'Dowex' Fine Mesh Resins

Manufactured by The Dow Chemical Company, Midland, Michigan.
Available from (1) The Dow Chemical Co.; (2) J. T. Baker Chemical Co.,
Phillipsburg, New Jersey; (3) Bio-Rad Laboratories, Berkeley, California;
(4) V. A. Howe and Co. Ltd., 26 Pembridge Road, London, W.11.

Designation	Type	Available particle size ranges (U.S. standard screens)
Dowex 50W-X1	Strongly acidic	50-100
-X2	cross-linked	50-100, 100-200, 200-400
-X4	polystyrene	20-50, 50-100, 100-200, 200-400
-X8	resins	20-50, 50-100, 100-200, 200-400
-X10		20-50
-X12		20-50, 50-100, 100-200, 200-400
-X16		20-50, 50-100
Dowex 1-X1	Strongly basic	50-100
-X2	cross-linked	50-100
-X4	polystyrene	20-50, 50-100
-X8	(Type I)	20-50, 50-100, 100-200, 200-400,
Dowex 21K		16-20, 20-50, 50-100
Dowex 2-X4	Strongly basic	20-50
-X8	cross-linked	20-50, 50-100
	polystyrene	
	resins	
	(Type II)	
Dowex 3	Weakly basic	
	cross-linked	
	polystyrene resin	20-50

The divinylbenzene content of a Dowex resin is indicated by an 'X number' following the number of the particular resin. For example Dowex 50-X4 is prepared from a styrene-divinylbenzene copolymer containing 4 per cent divinylbenzene. The particle size range '20-50' is that of the wet ion-exchange resin. The other particle size ranges are those of the copolymer spheres before the introduction of the ionic groups.

Table 5. Mixed bed ion-exchange resins

Designation	Manufacturer	Composition	Notes
Amberlite MB-1	Rohm and Haas Co.	{Amberlite IR-120 (H form) Amberlite IRA-400 (OH form)	
Amberlite MB-2	Rohm and Haas Co.	{Amberlite IR-120 (H form) Amberlite IRA-410 (OH form)	
Amberlite MB-3	Rohm and Haas Co.	{Amberlite IR-120 (H form) Amberlite IRA-410 (OH form)	{Contains a dye to indicate exhaustion
Bio-Deminrolit	The Permutit Co. Ltd., London	{Zeo-Karb 225 (H form) De-Acidite FF (OH form)	
Ionac-Bio-Demirolit	The Permutit Co. Ltd., London	{Zeo-Karb 225 (H form) De-Acidite FF (OH form)	{Contains a dye to indicate exhaustion

Commercial Ion-exchange Resins

A large number of different ion-exchange resins are available from the manufacturers but most of these resins belong to one of the four main types; strongly acidic, strongly basic, weakly acidic, and weakly basic. The properties of the commercial ion-exchange resins which are commonly employed in the laboratory are summarized in *Tables 3-5*. Most of these resins are available in forms specially suitable for use in the laboratory and can be obtained in different particle sizes and with different degrees of cross-linking.

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Chapter 3

PROPERTIES OF ION-EXCHANGE RESINS

If a dry ion-exchange resin is immersed in an aqueous electrolyte solution, water will be absorbed by the resin from the solution; some of the electrolyte may penetrate into the resin phase, and some of the exchangeable ions in the resin will be replaced by ions from the solution. Although all these phenomena will occur simultaneously it is most convenient, when describing the properties of ion-exchange resins, to consider first the swelling properties of the resins and then the phenomenon of electrolyte penetration under conditions where there is no exchange of different ions. This simplifies the consideration of ion-exchange equilibria and ion-exchange kinetics.

Swelling of Ion-exchange Resins

When immersed in water, dry ion-exchange resin particles swell to an extent which is determined by: (a) the nature of the resin matrix and in particular the degree of cross-linking; (b) the nature and concentration of the functional groups; and (c) the nature of the exchangeable ions, i.e. the 'form' of the resin. The effect of the degree of cross-linking is of special importance and the variation in the swelling of sulphonated cross-linked polystyrene resins (in the hydrogen form) with the divinylbenzene (DVB) content of the copolymer is shown in *Figure 12*¹. It will be seen that resins with a low DVB content have a high degree of swelling in water and that, as the proportion of the cross-linking agent is increased, the swelling is reduced. A resin with a high degree of swelling will occupy more space in a column than a similar resin with a low degree of swelling which has the same dry weight and the same exchange capacity in mg equivalents. This effect

INTRODUCTION

can be seen from *Figure 12* in which the exchange capacity in mg-equiv./ml. has also been plotted against the divinylbenzene content of the resin. Similar behaviour is observed with strongly basic anion-exchange resins; the resins with a low degree of cross-linking swell to a much greater extent in water than do the highly cross-linked resins and have a lower ion-exchange capacity on a volume basis. With both strongly acidic and strongly basic resins there is not usually any great change in the swelling in water when the resin is converted from one ionic form to another. If, however, the exchangeable ion is strongly absorbed by the resin the swelling is usually

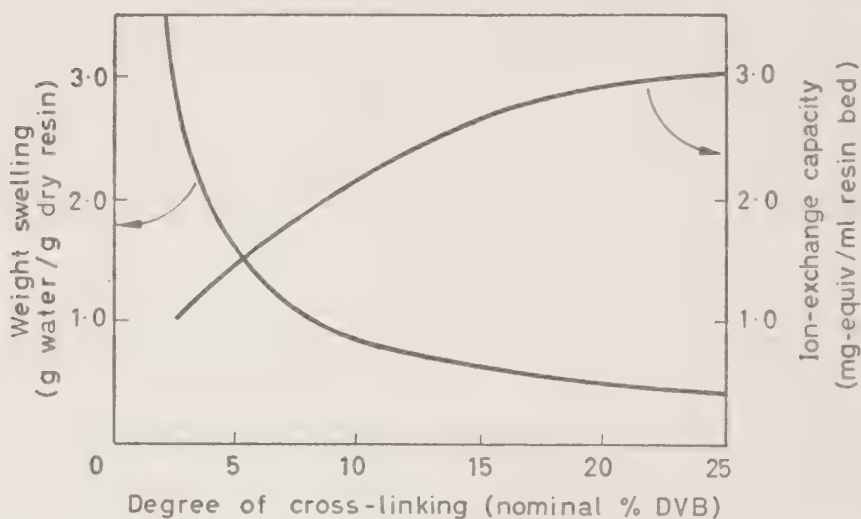


Figure 12. The effect of the degree of cross-linking of sulphonated polystyrene resins on the weight-swelling and the ion-exchange capacity of unit settled volume. (From K. W. Pepper¹, by courtesy of Transactions of the Plastics Institute)

less than when the resin is in the hydrogen or hydroxyl form. With weakly acidic and weakly basic resins the swelling in water is least when the resins are in the free acid or free base forms respectively, and there is usually a large increase in volume when resins of either type are converted to the salt form. The effect of the concentration of the functional groups on the swelling of ion-exchange resins is of little practical importance but, in general, for similar resins with the same

degree of cross-linking, the higher the concentration of functional groups the greater the swelling in water.

Electrolyte Penetration

If, instead of being immersed in water, a strongly acidic cation-exchange resin in the sodium form is immersed in a solution of sodium chloride it is often assumed that little or no sodium chloride is absorbed by the resin and that, as the only exchange process which takes place is between sodium ions in the solution and sodium ions in the resin, there is no change in the amount of sodium chloride in the solution. This is nearly true in dilute solution, but in more concentrated solutions appreciable amounts of sodium chloride will be present in the resin. Since the ionic groups which are attached to the polymer network cannot diffuse into the external solution but the exchangeable ions are free to do so, a particle of an ion-exchange resin may be considered as being surrounded by a semi-permeable membrane, which is permeable to the exchangeable ions but impermeable to the ionic groups. If the resin particle is in equilibrium with an electrolyte solution, the system can therefore be considered as a Donnan membrane equilibrium. In the case of a cation-exchange resin in the sodium form which is in equilibrium with a solution of sodium chloride, the approximate relationship between the concentration of the sodium and chloride ions in the resin and in the solution will be

$$\frac{(\text{Na}_R^+)}{(\text{Na}_S^+)} = \frac{(\text{Cl}_S^-)}{(\text{Cl}_R^-)}$$

where (Na_R^+) and (Cl_R^-) are the total concentrations of the sodium and chloride ions in the resin and (Na_S^+) and (Cl_S^-) are their corresponding concentrations in the solution.

Even with a resin of moderate cross-linking the concentration of sodium ions in the resin may be as high as 5 N. If the concentration of sodium and chloride ions in solution is 0.1 N, then the concentration of chloride ions in the resin will be 0.002 N. When the concentration of sodium chloride in the external solution is 1 N, however, the concentration of

chloride ions in the resin will be 0.2 N. In general, if a fully ionized resin is in equilibrium with a dilute solution of a strong electrolyte, very little of the electrolyte will be absorbed by the resin. At higher concentrations, however, the absorption may be appreciable. This effect is not observed with non-electrolytes and is very much less with weak electrolytes. Non-electrolytes may be strongly absorbed by ion-exchange resins even from dilute solution, and with weak electrolytes the absorption will normally be greater than with strong electrolytes².

Ion-exchange Equilibria

The ion-exchange process itself involves the replacement of the exchangeable ions in the resin by ions of like charge from a solution. If an ion-exchange resin containing exchangeable A ions is brought into contact with a solution containing B ions then the exchange process may be represented by the equation



A ions in the resin (A_R) are replaced by B ions from the solution (B_S) and since, as shown in the equation, this is a reversible process an equilibrium is eventually set up in which some of the A ions initially present in the resin have been replaced by B ions from the solution. The extent to which one ion is absorbed in preference to another is of fundamental importance in nearly all applications of ion-exchange resins; it will determine the efficiency of a process in which a resin is used to recover ions from dilute solution and the ease with which the ions can subsequently be removed from the resin, and it will also determine the readiness with which two or more substances, which form ions of like charge, can be separated by ion-exchange chromatography.

The distribution of ions between an ion-exchange resin and solution may depend on a large number of factors. The effects of some of the more important factors are summarized and described briefly in *Table 6*. Since some of the effects are complex it is, in general, impossible to predict the precise effect of many of these factors but the more fundamental features have been investigated in some detail.

Table 6. Some of the more important factors determining the distribution of ions between an ion-exchange resin and a solution

1. Nature of Exchanging Ions

(a) *Charge*

In dilute solution, ions carrying a high charge are more strongly absorbed than ions of lower charge. For example, bivalent ions are more strongly absorbed than univalent ions.

(b) *Size*

Large ions, especially organic ions, are often absorbed strongly, but the full exchange capacity may not be observed. Very large molecules, e.g. proteins, may not be able to penetrate into the resin structure and will be absorbed on the surface only.

(c) *Polarizability and hydration*

In general, the higher its polarizability and the lower its degree of hydration, the more strongly will an ion be absorbed.

2. Nature of Ion-exchange Resin

(a) *Nature of functional groups*

Resins containing weakly acidic and weakly basic groups are highly selective in their behaviour towards H^+ and OH^- ions. Hydrogen ions are, for example, strongly absorbed by carboxylic resins and hydroxyl ions by weakly basic anion-exchange resins. Resins containing carboxylic acid groups strongly absorb Ca^{++} and Cu^{++} ions. Strongly basic anion-exchange resins of Type II absorb hydroxyl ions more strongly than do the Type I resins. Ion-exchange resins containing groups which are capable of complex formation with particular ions will absorb these ions more strongly. For example, copper ions are absorbed by weakly basic anion-exchange resins containing amine groups which can form ammine complexes.

(b) *Degree of cross-linking*

In general, ion-exchange resins become more selective in their behaviour towards ions of different size (the volume

INTRODUCTION

of the ion is assumed to include water of hydration) as the degree of cross-linking is increased and the swelling decreased. The ion with the smaller hydrated volume will usually be absorbed preferentially.

3. Nature of Solution

(a) *Total concentration of exchanging ions*

The distribution of ions between resin and solution is affected by the total concentration of the ions in solution. If the ions involved in the exchange process carry the same charge this effect is relatively small but if the ions are of different charge then the effect may be large. For example, Ca^{++} ions are preferentially absorbed by a cation-exchange resin from a dilute solution containing Na^+ and Ca^{++} ions, but in more concentrated solution Na^+ ions are readily absorbed.

(b) *Nature of other ions or solutes in the solution*

With solutions of strong electrolytes, the distribution of the exchanging ions between the resin and the solution is not appreciably affected by the nature of non-exchanging ions in the solution. With solutions of weak electrolytes, or if other solutes are present which can form complexes with exchanging ions, then the effects of ionic equilibria in solution have to be considered. For example, the exchange process $\text{H}_R^+ + \text{Na}_S^+ \rightleftharpoons \text{Na}_R^+ + \text{H}_S^+$ is favoured if acetate (or hydroxyl) ions are present in the solution instead of, for example, chloride ions; the acetic acid (or water) formed will be only slightly dissociated and the hydrogen ion concentration in the solution will only increase slightly. A similar effect will be observed if other solutes are present which can form complexes with the ions in the resin and the reverse effect will be observed if complexes are formed with the exchanging ions present in the solution.

Most of the fundamental studies on ion-exchange equilibria have been carried out with relatively simple systems so that the basic principles can be more easily understood. If complicating effects, such as those due to the formation of complexes

in solution, are absent, then the distribution of the exchanging ions between the resin and the solution is determined by their concentrations in the resin and in the solution and by their relative affinities for the resin. The affinity of a single ion for an exchange group in a resin cannot be determined but the relative affinity for the resin of two ions which are competing for the same exchange site can be measured. If we consider the exchange of two univalent cations between a strongly acidic cation-exchange resin and a solution,



then the relative affinity of the two ions for the resin is usually expressed by the relationship

$$\frac{(B_R)}{(A_R)} = K_A^B \frac{(B_S)\gamma_B}{(A_S)\gamma_A} \quad \dots (1)$$

where (B_R) and (A_R) are the concentrations of the two cations in the resin, (B_S) and (A_S) their concentrations in solution, γ_B and γ_A the corresponding activity coefficients and K_A^B the relative affinity coefficient of the two ions. If activity corrections are not applied, we have the simpler relationship

$$\frac{(B_R)}{(A_R)} = K_{cA}^B \frac{(B_S)}{(A_S)} \quad \dots (2)$$

K_{cA}^B is known as the practical or 'stoichiometric relative affinity coefficient'. If K_{cA}^B is greater than unity then, if there are no complicating effects in solution, the resin has a greater affinity for ion B than ion A. If it is less than unity, the affinity for ion A is greater than for ion B. This simple relationship is of course obtained if the classical law of mass action is applied to the exchange equilibrium; more refined quantitative treatments involve the consideration of activity coefficient and swelling energy effects in the resin phase^{3,4}.

Equation (2) can also be written in the form

$$\frac{X_R^B}{1 - X_R^B} = K_A^B \frac{X_S^B}{1 - X_S^B} \quad \dots (3)$$

INTRODUCTION

where X_R^B and X_S^B are the equivalent fractions of the ion B in the resin and in the solution, i.e.

$$X_R^B = \frac{(B_R)}{(A_R) + (B_R)}$$

and

$$X_S^B = \frac{(B_S)}{(A_S) + (B_S)}$$

If K_{cA}^B is unity then X_R^B is always equal to X_S^B ; if K_{cA}^B is greater than unity then X_R^B is always greater than X_S^B , and if K_{cA}^B is less than unity then X_R^B is always less than X_S^B . Some results obtained with univalent cations are shown in *Figure 13*⁵.

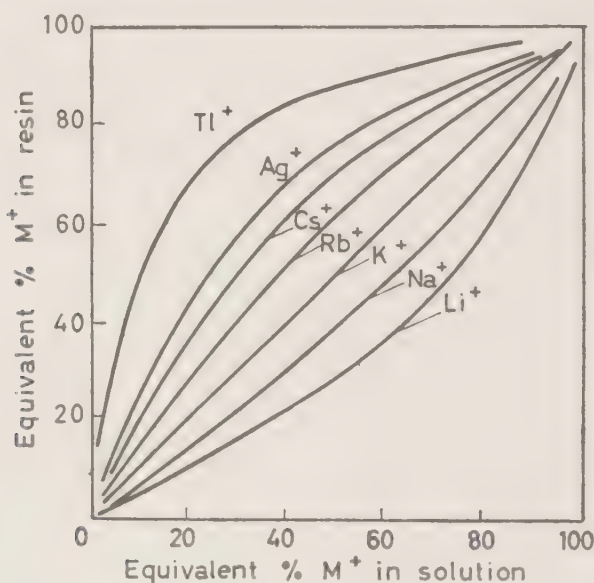


Figure 13. Cation exchange with a strongly acidic resin. Equilibrium with univalent cations. (From T. R. E. Kressman and J. A. Kitchener⁵, by courtesy of Journal of the Chemical Society)

The experiments were carried out with a strongly acidic cation-exchange resin in the ammonium form and solutions of the appropriate metal salts. It will be seen that $K_{cK}^{NH_4}$ is very nearly unity, i.e. the potassium and ammonium ions have nearly the same affinity for the resin, but that some of the other cations have a higher affinity for the resin than the ammonium ion and some have a lower affinity.

It follows from equation (2) that, if the ratio of the concentrations (or the equivalent fractions) of the two ions in the resin is plotted against the ratio of their concentrations in solution, a straight line should be obtained with a gradient which is equal to the relative affinity coefficient. When plotted in this way, the results obtained with a strongly acidic resin and univalent cations gave the approximately straight lines shown in *Figure 14*. This showed that with these ions

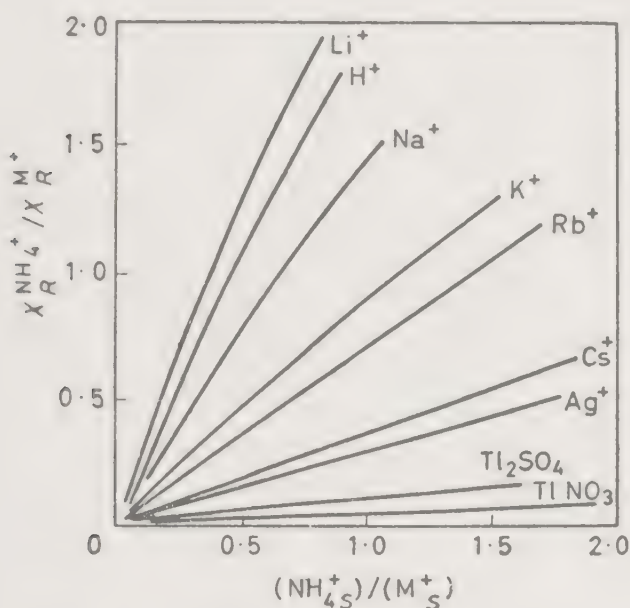
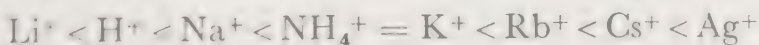


Figure 14. Cation exchange with a strongly acidic resin. Equilibria with univalent cations. (From T. R. E. Kressman and J. A. Kitchener⁶, by courtesy of Journal of the Chemical Society)

the relative affinity coefficient was nearly constant but varied slightly with the composition of the resin. It will be seen from *Figure 14* that, with the alkali metal, ammonium and silver cations, the order of affinity for the resin is



Thus with the alkali metal cations the affinity for the resin increases with decrease in the size of the hydrated ion. This order of affinity, which is observed with most of the common strongly acidic resins has been termed the 'natural order of

affinity'⁶. However, the relative affinity coefficient is not a constant which is characteristic of a particular pair of ions but also depends on the nature of the resin. With strongly acidic cation-exchange resins, both the degree of cross-linking and the composition of the resin have been shown to have a marked effect on the relative affinity coefficient⁶. The type of effect which has been observed is shown in *Figure 15* where the relative affinity coefficient K_{Na}^K for the exchange of potassium and sodium ions with strongly acidic sulphonated polystyrene resins of different degrees of cross-linking, has been plotted against the equivalent fraction of potassium ion in the resin. It will be seen that the lightly cross-linked resin containing 5½ per cent DVB shows a slight preference for the potassium ion and, as the degree of cross-linking is increased, this

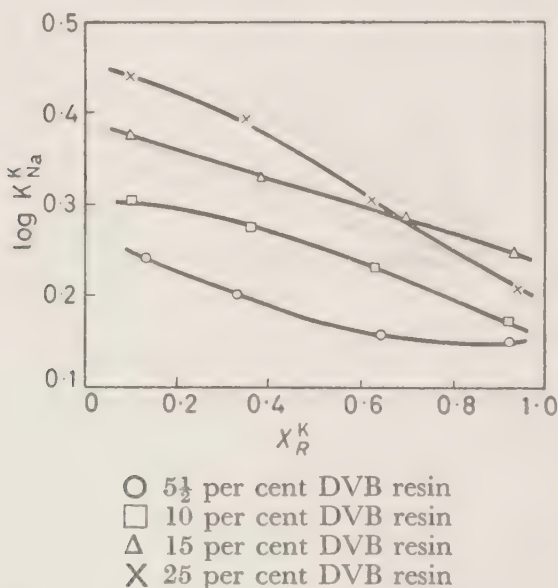


Figure 15. Potassium–sodium ion exchange with sulphonated cross-linked polystyrene resins of different degrees of cross-linking. (From D. Reichenberg and D. J. McCauley⁶, by courtesy of Journal of the Chemical Society)

preference increases, but that with a very highly cross-linked resin (25 per cent DVB) a low selectivity for potassium is observed when the resin is largely in the potassium form.

The exchange of univalent ions with anion-exchange resins has not been so thoroughly investigated but the behaviour of univalent anions appears to be very similar to the behaviour of univalent cations. With a strongly basic anion-exchange resin of Type I, the following order of affinity has been observed⁷,

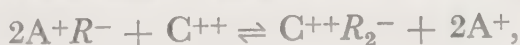


With a strongly basic resin of Type II, the order of affinity was,



It will be seen that the hydroxyl ion occupies a slightly higher position in the second series.

In exchange processes involving univalent ions only, the equilibrium is little affected by the total ionic strength of the solution. It will be noted that equation (3) does not involve any term corresponding to the total concentration of the ions in the resin or in the solution and K_{cA}^B is dimensionless. If, however, the law of mass action is applied to an exchange process in which uni- and bivalent ions are involved, e.g.



then we have the relationship

$$\frac{(\text{C}_R)}{(\text{A}_R)^2} = K_{cA}^C \frac{(\text{C}_S)}{(\text{A}_S)^2} \quad \dots (4)$$

where (C_R) and (A_R) are the concentrations of the ions in the resin and (C_S) and (A_S) are their concentrations in solution. If the same units (g-equiv./l. or mole/l.) are used to express the concentration of the ions in the resin and in the solution, then K_{cA}^C will be dimensionless but its value will depend on the units employed. Equation (4) may also be written in the form

$$\frac{X_R^C}{(1 - X_R^C)^2} = K_{cA}^C \frac{\text{C}_R}{\text{C}_S} \frac{X_S^C}{(1 - X_S^C)^2} \quad \dots (5)$$

where X_R^C and X_S^C are the equivalent fractions of the ion C in the resin and in the solution and C_R and C_S are the total concentrations of the exchanging ions in the resin and in the

INTRODUCTION

solution. Unlike equation (3), this equation involves the term C_R/C_S and the effective selectivity of the resin is determined by the value of $K_{cA}^C \left(\frac{C_R}{C_S} \right)$. Since C_R is determined by the exchange capacity (in g-equiv./l.) it will be fixed for a particular resin and, neglecting any small changes in swelling, it will not be affected by changes in the concentration of the external solution. The value of C_S , however, will depend on the total concentration of the ions in the solution. It follows that the value of X_R^C will depend not only on K_{cA}^C and X_S^C but also on C_S , and the effective selectivity of the resin for the divalent ion will be inversely proportional to the concentration of the solution, i.e. the relative absorption of the divalent ion will be much greater in dilute solution. The effect of solution concentration is also shown in *Figure 16* where the theoretical

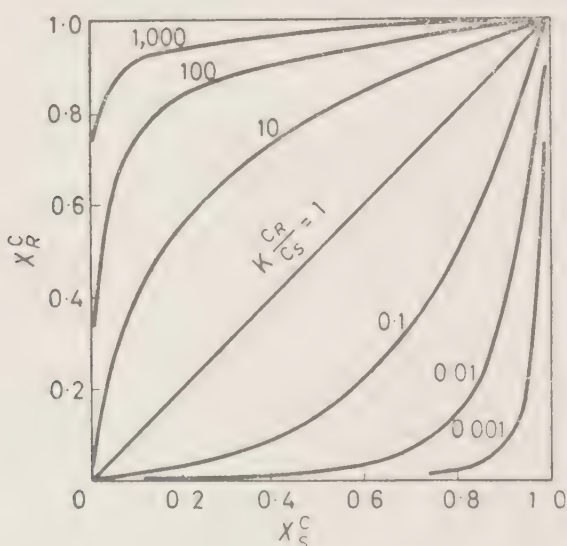
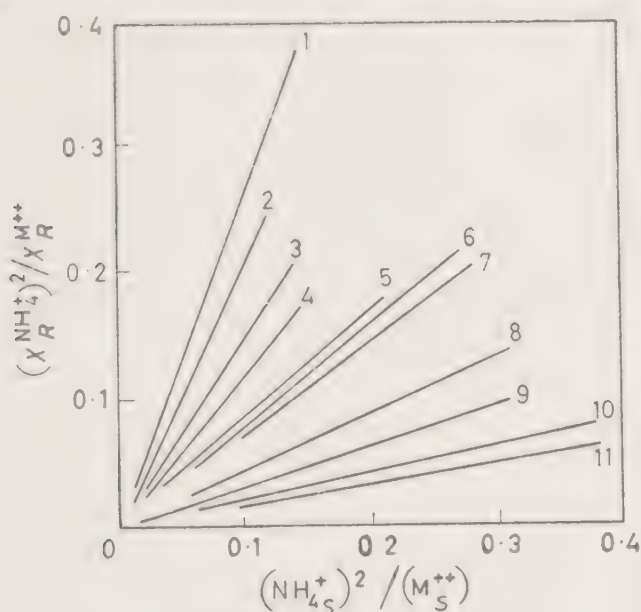


Figure 16. Cation-exchange equilibria with univalent-bivalent ion systems. Variation of X_R^C with X_S^C for different values of $K_{cA}^C C_R/C_S$

values of X_R^C have been plotted against X_S^C for different values of $K_{cA}^C C_R/C_S$. If the appropriate mass action functions are plotted, however, straight lines are obtained as shown in *Figure 17*. These results were obtained with a strongly acidic cation-exchange resin in the ammonium form and various

bivalent cations⁸. It will be seen that the order of affinity is $\text{Cd}^{++} < \text{Be}^{++} < \text{Mn}^{++} < \text{Mg}^{++} = \text{Zn}^{++} < \text{Cu}^{++} = \text{Ni}^{++} < \text{Co}^{++} < \text{Ca}^{++} < \text{Sr}^{++} < \text{Pb}^{++} < \text{Ba}^{++}$ but that in sulphate solution



- | | |
|---|--------------------------------|
| 1. CdCl_2 | 7. CoCl_2 |
| 2. BeSO_4 | 8. CaCl_2 |
| 3. MgSO_4 | 9. SrCl_2 |
| 4. MnSO_4 | 10. $\text{Pb}(\text{NO}_3)_2$ |
| 5. MgCl_2 ; $\text{Mg}(\text{NO}_3)_2$; ZnCl_2 | 11. BaCl_2 |
| 6. CuCl_2 ; NiCl_2 | |

Figure 17. Cation exchange with a strongly acidic resin. Equilibria with bivalent cations. (From T. R. E. Kressman and J. A. Kitchener⁸, by courtesy of Journal of the Chemical Society)

magnesium has an apparently lower affinity for the resin than in chloride solution. From these results it was concluded that with bivalent ions the ionic size (as measured by the distance of closest approach in solution) was a determining factor but that the incomplete dissociation of the salts of bivalent metals in solution also had an important effect on the extent of exchange.

In exchange processes involving univalent and tervalent ions, the effect of the ionic strength of the solution is much greater. In this case the equivalent fraction of the tervalent ion in the

resin will be inversely proportional to the square of the total solution concentration.

The ease and efficiency with which ion-exchange resins can be used for softening hard water depends very largely on the effect which has been described above. The bivalent calcium and magnesium ions are readily removed from the hard water (i.e. from dilute solution) and can then be easily displaced from the resin by the sodium ions in a concentrated sodium chloride solution. In the demineralization of water the bivalent cations are readily removed from the resin by the use of a concentrated acid solution as the regenerant.

Similar effects are observed with anion-exchange resins: polyvalent anions are preferentially absorbed from dilute solution. It must be remembered, however, that most polybasic acids dissociate in stages, and that the degree of dissociation will depend on the concentration and extent of neutralization. Anions of different valency may be present in the solution, and these will be absorbed by the resin to an extent determined by their affinity for the resin, their relative concentration and the total concentration of the solution. Sulphuric acid in dilute solution, for example, is absorbed largely as sulphate ions SO_4^{--} which would be expected to be absorbed preferentially by anion-exchange resins under these conditions. In concentrated solutions, on the other hand, the sulphuric acid is absorbed largely in the form of univalent bisulphate ions HSO_4^- ^{9,10}.

The same general principles apply to the exchange of organic ions on ion-exchange resins. The affinity of organic ions may be very high, presumably owing to the effect of van der Waals forces; but with large organic ions there may be insufficient space available within the resin structure for the absorption of an organic ion at each exchange site even under favourable conditions¹¹. Very large molecules, such as proteins, will be absorbed only on the outside surface of the resin particles. Proteins can thus be separated from amino acids by 'ionic sieve' effect.

Ion-exchange Kinetics

The rate at which an ion-exchange equilibrium is approached is often of considerable practical importance. If the rate of

exchange is low a long time is required for the attainment of equilibrium between resin and solution; as will be seen later this means that, in column experiments, slow flow rates have to be employed and ion-exchange procedures become lengthy and tedious.

In the exchange reaction



five steps can be considered to be involved in the exchange process:

- (1) the diffusion of B^+ ions through the solution up to the surface of the ion-exchange resin particles;
- (2) the diffusion of B^+ ions through the resin particles to the exchange site;
- (3) the replacement of A^+ ions by B^+ ions at the exchange site;
- (4) the diffusion of A^+ ions back through the resin particles towards the solution;
- (5) the diffusion of A^+ ions away from the surface of the resin particles into the bulk solution.

All of these processes will of course occur simultaneously. It is usually assumed that electroneutrality is maintained in the resin and in solution during ion exchange, so that processes (1) and (5), and processes (2) and (4) are linked. In effect therefore only three processes are involved:

- (a) the diffusion of B^+ ions up to the surface of the resin particles and the simultaneous diffusion of A^+ ions away from the resin surface;
- (b) the diffusion of B^+ ions through the resin structure towards the exchange site and the simultaneous diffusion of A^+ ions back through the resin towards the solution;
- (c) the replacement of A^+ ions by B^+ ions at the exchange site.

Although all these processes occur simultaneously any one may be rate controlling, i.e. the overall rate of exchange may depend on the rate of one of these processes which is proceeding more slowly than the others. No case has yet been found where process (c), sometimes called the chemical pro-

INTRODUCTION

cess, is rate controlling and the overall rate of exchange is therefore normally controlled by processes (a) or (b).

The rate of process (a) will depend on the degree of mixing in the external solution. If the resin particles are stirred with the solution, or if the solution is allowed to flow past the resin particles in a column, good mixing may be achieved in the bulk solution, but for hydrodynamic reasons, in the neighbourhood of the surface of the particles, mixing will be imperfect. In other words, it is impossible for the solution to be mixed perfectly right up to the surface of the resin particles. The hydrodynamics of the mixing process are complex but, as an approximation, the bulk solution can be considered to be thoroughly mixed and the resin particles can be considered to be surrounded by a thin film of completely unstirred solution. The thickness (δ) of this film will then depend on the degree of agitation in the solution. Since the bulk solution is assumed to be perfectly mixed, process (a) will depend on the diffusion of the ions through this surface film and this process is therefore usually known as 'film diffusion'. This concept of a thin film of static solution was first introduced by Nernst and the film is often known as a Nernst film or a Nernst diffusion layer. The rate of film diffusion is increased by

- (i) reducing the thickness (δ) of the Nernst film by increased agitation;
- (ii) increasing the concentration of the exchanging ions in the solution;
- (iii) decreasing the particle size of the resin, i.e. increasing the surface area; or
- (iv) increasing the temperature.

Process (b) which involves the diffusion of ions through the resin structure is usually known as 'particle diffusion'. If the rate of film diffusion is sufficiently high, the surface of the resin particles will be almost in equilibrium with the solution and the rate of particle diffusion will be determined solely by the conditions inside the resin particles. The rate of particle diffusion is therefore increased by

- (i) increasing the 'porosity' of the resin, i.e. decreasing the degree of cross-linking;
- (ii) decreasing the particle size of the resin; or
- (iii) raising the temperature.

The parts played by these two diffusion processes are shown diagrammatically in *Figure 18*.

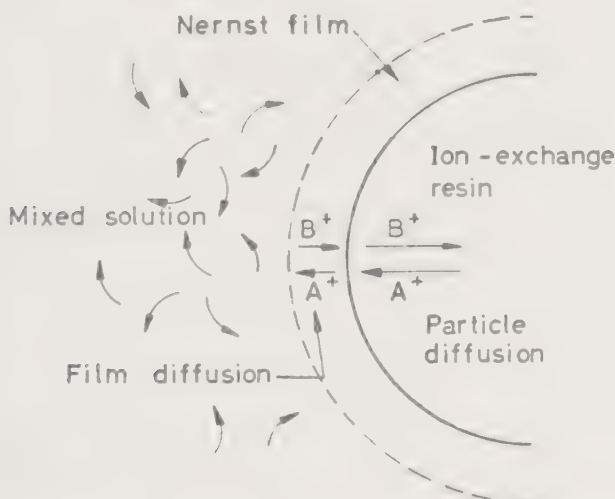


Figure 18. Ion-exchange kinetics. Film diffusion and particle diffusion processes

Studies on ion-exchange kinetics^{12,13} have shown that the nature of the rate-controlling process is determined by the relative effects of the diffusion coefficients, the film thickness and the particle size on the two diffusion processes. Boyd, Adamson and Myers¹² showed that with a given system the conditions under which particle or film diffusion was rate controlling were determined by the ratio

$$\frac{\pi^2 D_R \delta k}{3 D_S r}$$

where D_S and D_R are the diffusion coefficients in the solution and in the resin, r is the radius of the particles, δ is the thickness of the diffusion layer and k is equal to $(B_R^+)/(B_S^+)[(B_R^+)$ and (B_S^+) are the final equilibrium concentrations]. If the ratio is less than unity then particle diffusion is the rate-controlling process; if it is greater than unity, then the rate is controlled by film diffusion.

INTRODUCTION

It has been found that with strongly acidic and strongly basic resins the rate of exchange of small ions at a low concentration in solution is normally controlled by film diffusion; at high solution concentrations, however, the rate-controlling process is usually particle diffusion. The rate of exchange with multivalent ions is more likely to be controlled by particle diffusion than is the rate of exchange with univalent ions. Large organic ions usually exchange very slowly and the rate is controlled by particle diffusion at all concentrations. Under conditions where particle diffusion is the rate-controlling mechanism, the degree of cross-linking of the resin has a marked effect on the rate of exchange; as the degree of cross-linking is increased, the exchange rates decrease.

The kinetics of exchange in the case of weakly acidic and weakly basic resins appear to be very similar except with exchange processes involving hydrogen or hydroxyl ions; these proceed very much more rapidly with strongly acidic or strongly basic resins. This difference in behaviour is due to differences in the degree of dissociation. The diffusion rate of the hydrogen ions in a weakly acidic resin, for example, is low because the concentration of hydrogen ions is small. As a result the rate-controlling process is 'particle diffusion' of hydrogen ions¹⁴.

In practical applications, slow rates of exchange often impose a serious limitation on the usefulness of the ion-exchange process. With a given system the only ways in which the rate of exchange can be increased are by: (a) reducing the particle size of the resin; (b) raising the temperature, or (c) reducing the degree of cross-linking of the resin, if particle diffusion is the rate-controlling process.

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Chapter 4

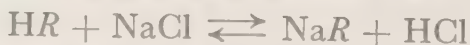
BEHAVIOUR OF ION-EXCHANGE COLUMNS AND ION-EXCHANGE CHROMATOGRAPHY

WHEN ion exchange is used in the laboratory for the treatment of solutions, a column of resin is usually employed. A glass tube is filled with a slurry of resin particles in water—ensuring that there are no air bubbles in the bed of resin—and then the solution to be treated is passed downwards through the column. In simple procedures of this type, ions in the solution which is passed through the column, are merely replaced by ions from the resin. In ion-exchange chromatography, a column of exchange material is used for the separation of substances which form ions of like charge in solution; in principle, the procedures are very similar to those used in other types of chromatography but there are important differences in practice.

The success or failure of an ion-exchange experiment may depend as much on the way in which the column is prepared and used as on the proper selection of the ion-exchange resin, and some understanding of the principles underlying the operation of ion-exchange columns can be of considerable help in the application of ion-exchange methods in the laboratory.

Simple Procedures

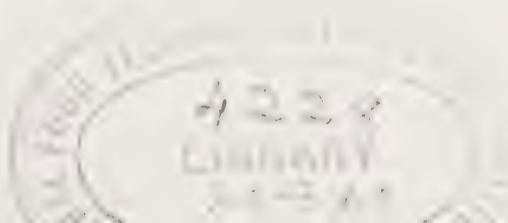
If a solution of sodium chloride is stirred with a strongly acidic cation-exchange resin in the hydrogen form, equilibrium will be rapidly attained and the sodium chloride will be partially converted into hydrochloric acid:



The extent of exchange will depend on the relative affinities of the sodium and hydrogen ions for the resin and on the

relative amounts of resin and sodium chloride solution but, unless an impracticably large excess of resin is used, exchange will be far from complete. The solution can, however, be separated from the partially exhausted resin and treated with a further quantity of fresh resin in the hydrogen form. Then, if this process is repeated a sufficient number of times, the sodium chloride can be quantitatively converted into hydrochloric acid by the use of far less resin than would be required if the conversion were attempted in a single stage. This process of repeated treatment with the resin can, in effect, be carried out automatically in an ion-exchange column. If a solution of sodium chloride is passed continuously down through a column of hydrogen form resin, the solution is repeatedly brought into contact with fresh resin, and the exchange process is carried to completion, easily and efficiently. After the sodium chloride solution has been passed through the column for a short time, the upper part of the resin bed will contain exhausted resin in the sodium form. The sodium chloride solution will pass unchanged through this part of the bed but further down the column it will enter a region, the 'exchange zone', where the sodium ions in the solution are quantitatively replaced by hydrogen ions from the resin. The hydrochloric acid produced then passes through the lower part of the column, which contains resin in the hydrogen form, and comes out of the bottom of the column at a concentration equivalent to that of the influent sodium chloride.

On continuing to pass sodium chloride solution, the exchange zone will move down the column as shown diagrammatically in *Figure 19*. In this figure, the diagrams represent different stages in the process. On the left and right of each diagram, the concentrations (C_s) of sodium and hydrogen ions in the effluent and influent have been plotted against the volume of solution (V) passed through the column. In the centre of each diagram, the concentrations of the ions in the column have been plotted against the distance (l) up the column. The diagrams show the concentrations both in the solution (C_s) and in the resin (C_R); normally, the concentration in the resin will, of course, be very much higher than in solution.



INTRODUCTION

The first diagram represents the initial state of the column; in the second diagram, the exchange zone is approximately half way down the column, and hydrochloric acid has appeared in the effluent. The rate at which the exchange zone moves down the column will be determined by the flow rate,

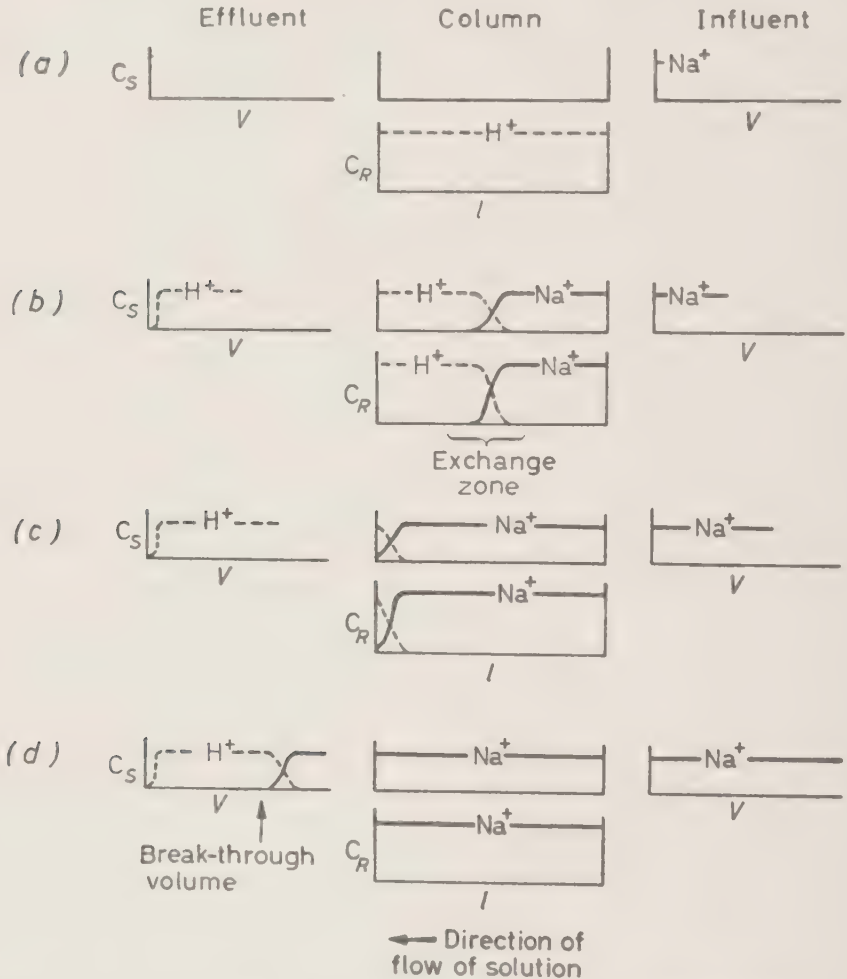


Figure 19. Behaviour of ion-exchange columns. Displacement of H^+ ions by Na^+ ions in a cation-exchange column

the exchange capacity of the resin, and the concentration of the influent sodium chloride solution. When the exchange zone reaches the bottom of the column, sodium chloride will just be on the point of appearing in the effluent as shown in Figure 19(c) and 'break-through' will take place. The concentration of sodium

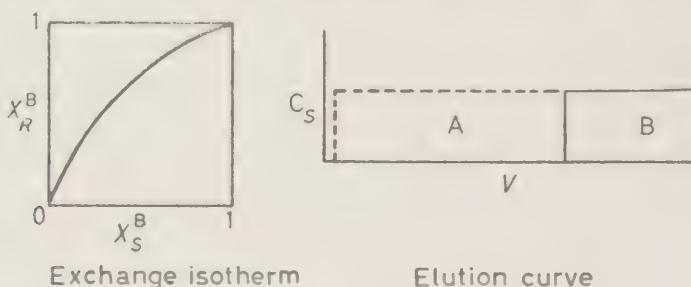
chloride in the effluent will then rise until it is the same as that in the influent, and at the same time the concentration of hydrochloric acid will fall to zero. When this stage has been reached, the exchange zone will have disappeared from the column and, as shown in *Figure 19(d)*, the resin will be completely in the sodium form. The volume of solution which has been passed through the column when 'break-through' occurs is known as the 'break-through volume'. The 'break-through capacity' is obtained by multiplying this volume by the concentration of the solution and is usually rather less than the total ion-exchange capacity of the column. In the example under consideration, the total ion-exchange capacity can be determined by three methods: (a) measuring (by titration) the amount of hydrogen ion displaced from the resin; (b) determining the difference between the amount of sodium ion passed into the column and the amount which is not retained by the resin (account should of course be taken of any sodium chloride solution remaining in the column); and (c) eluting the absorbed sodium ion with, for example, hydrochloric acid and determining the sodium ion in the eluate.

Ideally, when a solution is passed through an ion-exchange column, the resin and solution should always be in equilibrium at any point in the column, i.e. 'local equilibrium' should be attained. Then, as the composition of the solution changes, ions should be absorbed or desorbed instantaneously by the resin so that, at any point, the resin and solution are always in equilibrium. In practice however, although local equilibrium can be closely approached with finite flow rates of solution, it can never be completely achieved for the following reasons: first, the resin particles have a finite size and secondly, equilibrium between resin and solution is not attained instantaneously (the rate at which exchange occurs may be determined by either particle diffusion or film diffusion as described in Chapter 3). In addition, ideal conditions cannot be attained in practice because some mixing will take place in the solution as it flows past the resin particles, some 'longitudinal diffusion' of the ions will occur and, because of irregularities in the packing, the solution may not flow in a uniform manner down the column ('channelling'). These

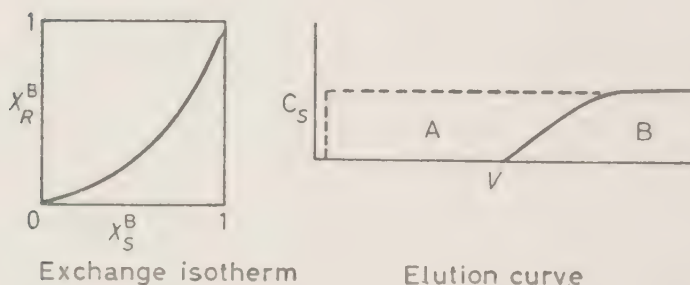
INTRODUCTION

various influences which prevent the attainment of ideal conditions can be described as 'disturbing factors'.

The form of the boundary between two exchanging ions in a solution passing down an ion-exchange column is determined by: (a) the ion-exchange isotherm and (b) the effects of the various disturbing factors. If the A ions initially



(a) Ion B absorbed more strongly than ion A



(b) Ion B absorbed less strongly than ion A

Figure 20. Replacement of ions in an ion-exchange column under ideal conditions. Ion-exchange isotherms and elution curves

in the resin are less strongly absorbed than the B ions in solution a 'self-sharpening' boundary will be obtained when the A ions are displaced from the resin by the passage of a solution containing the B ions. This sharp boundary will move down the column at a constant speed determined by the flow rate and, if the concentration of the ions in the effluent is plotted against the effluent volume, an 'elution curve' of the form shown in *Figure 20(a)* will be obtained. The A ions are

displaced from the column without any overlap of the concentrations of the A and B ions. The exchange isotherm for the Na-H system is of the form shown in *Figure 20(a)* and, under favourable conditions, an elution curve of the type shown is obtained. The self-sharpening tendencies of the boundary counteract the effects of the disturbing factors which tend to make the boundary diffuse. Under less favourable conditions, the influence of the disturbing factors is predominant and a diffuse boundary of the form shown in *Figure 19* is obtained.

If the A ion is more strongly absorbed than the B ion, i.e. the exchange isotherm is of the form shown in *Figure 20(b)* then a 'self-diffusing' boundary is obtained. As the boundary moves down the column it continually decreases its slope and an elution curve of the type shown in *Figure 20(b)* is obtained. In practice, the boundary may be even more diffuse as a result of the effects of the disturbing factors.

In practical applications it is of considerable advantage if a sharp boundary is obtained and when a choice of conditions is available, it is best to use those which lead to a sharp boundary. This will mean that a smaller column and higher flow rates can be used. Sometimes, however, it may be impossible to avoid diffuse boundaries. In analytical work, where quantitative exchange is essential (e.g. in the determination of salts as their corresponding acids), it is advisable to use an adequate excess of resin so that, if a diffuse boundary is formed, premature break-through may be avoided. When multivalent ions or organic ions are involved in the exchange process, the rates of exchange are low; diffuse boundaries are therefore likely to be formed and may lead to practical difficulties when the ions are being absorbed or desorbed. These difficulties can be reduced by (a) decreasing the flow rate of the solution; (b) decreasing the particle size of the resin; (c) decreasing the degree of cross-linking; or (d) increasing the temperature. The adjustment of any of these variables in the way described is likely to result in a closer approach to the ideal condition of perfect local equilibrium.

Ion-exchange Chromatography

Complex mixtures of closely related substances, e.g. rare earths or nucleic acid degradation products, are frequently separated or analyzed by ion-exchange chromatography. The procedures used are very similar to those employed in other types of chromatography but 'liquid chromatography' is invariably employed. Although the actual separation takes place in the column itself, the effluent from the column is analyzed or collected in fractions, so that the separate constituents of the mixture can be isolated.

In principle, however, the methods are very similar to those used in adsorption or partition chromatography. Three types of chromatographic procedure have been distinguished by Tiselius, and this classification can also be used in ion-exchange chromatography. The three procedures are: (a) frontal analysis; (b) displacement development; and (c) elution.

These methods of separation are described below and the differences between the three procedures are also shown in *Figure 21*, in which the concentrations of the ions in the column effluent (C_s) have been plotted against the effluent volume (V).

Frontal analysis

In frontal analysis, a solution containing the ions to be separated is passed through a column of an ion-exchange resin containing exchangeable ions which are less strongly absorbed than any of those in the mixture. The ions initially in the resin are therefore displaced down the column in front of the ions in the mixture. Under these conditions, the more strongly an ion is absorbed by the resin the less rapidly will it move down the column. The least strongly absorbed ions therefore accumulate in an absorption band which moves down the column in front of the other ions in the mixture.

Figure 21(a) shows the changes in the concentrations of the ions in the column effluent when a solution containing A ions and B ions is passed through a column of resin in the C form. In the influent, the concentration of the B ions (in g equiv./l.) is twice that of the A ions. Both the ions in the mixture are assumed to be absorbed more strongly than the C ions, and

the B ions more strongly than the A ions. After the water initially present in the column has been displaced, the concentration of C ions in the effluent rises sharply to a value equal to the total concentration of ions in the influent solution. When the C ions have been displaced from the column, the absorption band which contains the less strongly absorbed A

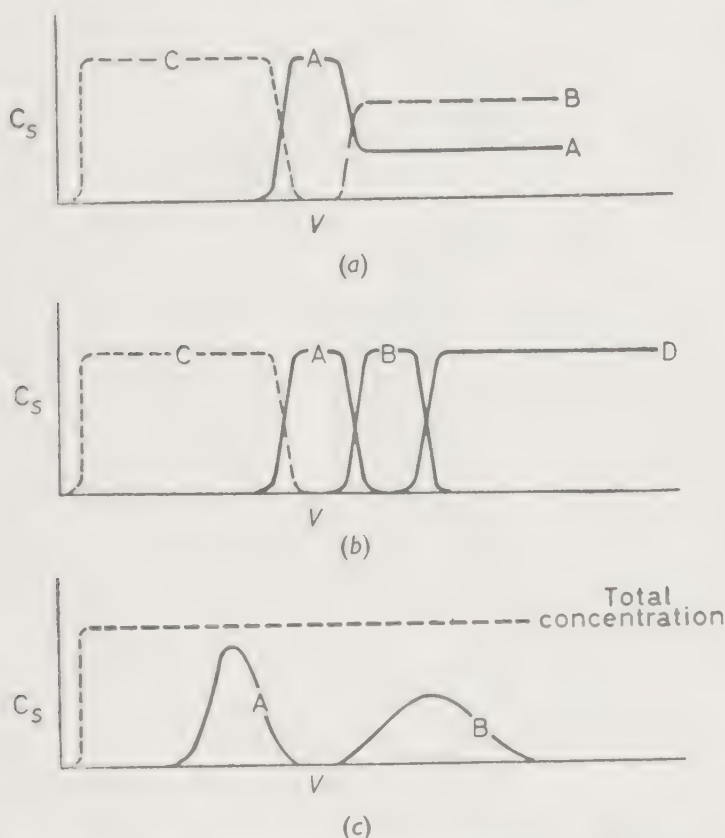


Figure 21. Ion-exchange chromatography: (a) frontal analysis; (b) displacement development; (c) elution

ions appears in the effluent; the volume of solution which contains A ions only will depend on the relative absorption of the A and B ions by the resin. On continuing to pass the solution through the column, B ions will appear in the effluent; the concentration of these ions will rise sharply and at the same time the concentration of the A ions will fall until the composition of the effluent solution is identical with that of the influent.

In frontal analysis, only one of the constituents in the mixture is separated from the others. This method, therefore, is not often employed but is useful occasionally for the removal of strongly absorbed impurities from a solution containing a solute which is only weakly absorbed.

Displacement development

In this procedure, a quantity of solution containing the mixture of ions to be separated is first passed through a column of resin in which the exchangeable ions are less strongly absorbed than any of the ions in the mixture. Provided an adequate excess of resin is employed, the mixture of ions will be absorbed in a well-defined band at the top of the column. Usually, the band occupies about 5–10 per cent of the length of the column but sometimes column loadings as high as 50 per cent are employed. In the next stage, a solution containing ions which, under the conditions employed, are more strongly absorbed than any of the ions in the mixture, is passed through the column. As the ions in the mixture are displaced down the column, they accumulate in contiguous bands. The lower bands contain the less strongly absorbed constituents, the upper bands the more strongly absorbed constituents.

The separation of A and B ions by displacement development with a resin in the C form and using a solution containing D ions as the displacement developer is shown in *Figure 21(b)*. It will be seen that, after the C ions have been displaced from the column, the A and B ions appear successively in the effluent at a concentration equal to that of the D ions in the influent solution. When the ions in the mixture have been displaced from the column, the concentration of D ions in the effluent rises sharply until it is equal to that in the influent solution. If the effluent from the column is collected in small fractions, some of the fractions will contain A ions only and some will contain B ions. Using displacement development, it is therefore possible to isolate each of the separate constituents of a mixture in a pure state. The method is particularly suitable for preparative purposes since the concentration of the ions in the effluent solution is high and the constituents of the mixture can be easily isolated. However, since

the bands which are formed in the column are contiguous, some of the effluent fractions will contain mixtures of two ions and none of the components in the mixture will be separated quantitatively. In preparative work, the fractions containing mixtures can be set aside for further treatment, but this procedure is, of course, unsuitable for the quantitative analysis of a mixture.

Elution

The procedure known as elution is very similar to displacement development but in this case, after the ions have been absorbed in a band at the top of the ion-exchange column, a solution containing ions which are less strongly absorbed than any of those in the mixture, is passed through the column. The exchanging ions in the eluting solution are frequently, but not necessarily, identical with those initially in the resin.

In elution, much lower column loadings are normally used than in displacement development. The initial band may occupy about 1–5 per cent of the column but in analytical work (e.g. the separation and analysis of amino-acid mixtures) very much lower column loadings may be employed. When the eluting agent is passed through the column, some of the exchanging ions in the solution pass through the band containing the mixture of ions to be separated. The ions in the mixture are drawn down the column and bands containing the separate constituents are formed. These bands usually have diffuse upper and lower boundaries although a sharp leading edge is sometimes observed, and they move down the column at rates which depend on the readiness with which the different ions are absorbed by the resin. During their progress down the column, the degree of separation between the bands increases but, at the same time, they become more diffuse.

Figure 21(c) shows the changes in concentration of the ions in the column effluent when a solution containing C ions is employed to separate a mixture containing A and B ions by elution using a column initially in the C form. The concentration of the C ions in the effluent is not plotted in this diagram but will be equal to the difference between the sum

of the concentrations of the A and B ions and the total concentration of the exchanging ions in the effluent. With an elution procedure, the constituents in a mixture can be completely separated. This method is therefore particularly suitable for quantitative analysis and is used extensively for the analysis of the complex mixtures of amino acids which can be obtained by the hydrolysis of proteins.

A large excess of the eluting agent is usually present in the effluent fractions and the concentration of the separated ions is relatively low. This means that this procedure is not generally as suitable for preparative work as displacement development; it has been used, however, for the isolation of rare earths and transuranium elements.

Since elution procedures are widely used in ion-exchange chromatography, the theoretical treatment of this process has assumed some practical importance. The simplest case arises when the exchange isotherms are linear; in elution procedures, the concentrations of the ions being separated are usually relatively low, and the exchange isotherms under these conditions are approximately linear. For example, in the case of uni-univalent exchange, as shown in Chapter 3, we have the relationship

$$\frac{X_R^B}{1 - X_R^B} = K_{cA}^B \frac{X_S^B}{1 - X_S^B} \quad \dots (1)$$

where K_{cA}^B can be assumed to be approximately constant. If X_R^B and X_S^B are very small compared with unity then

$$X_R^B \simeq K_{cA}^B X_S^B$$

and we have a linear relationship between the concentration of an ion in the resin and its concentration in solution. For this case of a linear isotherm, Mayer and Tompkins¹ developed a simple theoretical analysis which was very similar to that developed previously by Martin and Synge² for partition chromatography. The ion-exchange column was assumed by Mayer and Tompkins to be analogous to a distillation column and was considered to consist of a number of 'theoretical plates' within each of which equilibrium was attained between resin and solution. In the plate theory, allowance is made for the

influence of the various disturbing factors, and for the non-attainment of equilibrium, by assuming that the solution has to pass through a finite length of the column before equilibrium is reached between the resin and the solution. The efficiency of a column can then be expressed either in terms of the effective height of the theoretical plate (EHTP) or in terms of the number of plates in the column. In their theory, Mayer and Tompkins assumed that the processes occurring in each plate took place in stages: a small volume of solution entered a theoretical plate, equilibrium was attained between the solution and the resin, and the solution then passed on to the next plate. Glueckauf³ developed a rather more accurate treatment in which this discontinuous flow treatment was replaced by a continuous flow model. The column was still considered to be divided into finite sections but the solution passed continuously from one section to the next. This treatment accounts satisfactorily for the bell-shape of the bands which, as shown in *Figure 21*, are usually observed in elution procedures when the concentration of the ions being separated is relatively low. It follows⁴ from the theories of Mayer and Tompkins¹ and of Glueckauf³ that the volume of eluting agent, \bar{V} , required to elute the maximum of a peak is given by

$$\bar{V} = K_d \times (\text{mass of resin in the column}) + V_0$$

where V_0 is the volume of water or solution initially present in the column, i.e. the interstitial volume, and K_d , the distribution coefficient, is defined by the equation,

$$K_d = \frac{(\text{amount of solute on resin}) \times (\text{volume of solution})}{(\text{g resin}) \times (\text{amount of solute in solution})}$$

The concentration (C) of an ion in the effluent is given by the relationship

$$C = C_{\text{max.}} \exp \left\{ \frac{-N}{2} \frac{(\bar{V} - V)^2}{\bar{V}V} \right\}$$

where N is the number of theoretical plates in the column, V is the volume of solution which has passed through the column

INTRODUCTION

and \bar{V} is the volume of solution required for the elution of the peak. The value of $C_{\max.}$, the concentration at the peak of the elution, is given by

$$C_{\max.} = \frac{m}{V} \sqrt{\frac{N}{2\pi}}$$

where m , the total amount of the ion, can be obtained from the area under the elution curve. The number of theoretical plates in the column can be obtained from the bandwidth (β) at the concentration $C_{\max.}/l$, by making use of the relationship

$$N = 8 \left(\frac{\bar{V}}{\beta} \right)^2$$

or from the height and area of the elution curve, by applying the equation

$$N = 2\pi \left(\frac{C_{\max.} V}{m} \right)^2$$

Glueckauf⁵ has shown how this theory may be used, for example, to calculate the best conditions for the separation of small quantities of sodium and potassium by elution. It is necessary, however, to make several assumptions when estimating the effects of the various disturbing factors. This means that, in practice, the theory has not often been used to predict precisely the best conditions for a separation. When some data has been obtained on the chromatographic behaviour of a mixture, the 'plate theory' can be very useful for the quantitative assessment of the results and as a guide to improvements in the method of separation.

It is important to note that the rate at which a band moves down the column is inversely proportional to the distribution coefficient of the ions in the band, and that the rate at which two peaks separate in the column is determined by the ratio of the two corresponding distribution coefficients. This ratio is the 'separation factor', and can be determined by batch experiments in which a quantity of the resin is shaken with a solution containing the two ions. As explained in Chapter 3, the distribution of ions between resin and solution

may depend not only on the relative affinities of the ions for the resin but may also be affected by the presence of complexing agents in the solution. By adding a complexing agent to a solution, the ratio of the distribution coefficients of two ions may be considerably increased. As a result of this increase in the separation factor, the ions may be separated much more easily by ion-exchange chromatography when a solution containing a complexing agent is used for elution. As the difference between the distribution coefficients is increased, however, the amount of eluting agent required for the elution of the more strongly absorbed component will also increase and may become impracticably high. In practice therefore, a compromise must be made or two eluting agents used in succession, so that the more strongly absorbed component may be recovered from the column in a reasonably small volume of solution. With a complex mixture the separation may be facilitated by the use of a series of eluting agents or the process known as 'gradient elution' may be used. In this process, the composition of the eluting solution is changed continuously. This procedure reduces the 'tailing' which is often observed in ion-exchange chromatography and eliminates the possibility of false peaks which may be observed in the elution curve when there is a sudden change in the composition of the eluting agent.

When attempting to separate a mixture of ions by elution chromatography, the general objectives should therefore be:

- (1) to choose conditions such that there are large differences between the distribution coefficients of the various ions in the mixture;
- (2) to use a column of sufficient length under conditions, so that the EHTP of the column is small enough to obtain a satisfactory separation. The EHTP can usually be decreased by reducing the flow rate and the particle size of the resin. Before attempting a separation by ion-exchange elution, the preliminary determination of K_d values has been recommended¹. The K_d values can be obtained by measuring the distribution of a small amount of solute (less than 0.1 mg-equiv./g of resin) between a weighed amount

INTRODUCTION

of the resin and a known volume of eluting solution when the resin has attained equilibrium with the solution. After a few experiments of this kind, it should be possible to select an eluting solution which will give a good separation factor and distribution coefficients in the range 2-30.

In this chapter it has only been possible to give a brief outline of the principles of ion-exchange chromatography but most of the procedures have now been fully treated theoretically and the effects of the various disturbing factors have been discussed in some detail⁵.

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Chapter 5

ION-EXCHANGE TECHNIQUES AND APPARATUS

A SHORT general account is given in this chapter of the different ways in which ion-exchange resins can be used in the laboratory. The applications of ion-exchange resins are now so numerous, and so diverse in nature, that they cannot all be included in a simple classification; the more important, however, may be classified as shown in *Table 7*. In all these

Table 7. Application of ion-exchange resins in the laboratory

A. *Replacement of ions*

(1) Replacement of cations or anions

(a) Analytical applications

(i) Quantitative replacement of ions which are difficult to estimate

(ii) Removal of interfering ions

(b) Preparation of acids, bases, and salts

(c) Concentration and recovery of ions from dilute solution

(2) Replacement of cations and anions

(a) De-ionization of water

(b) De-ionization of solutions of non-electrolytes

B. *Separation of mixtures of ions by ion-exchange chromatography*

(1) Separation of mixtures of cations or anions

(2) Separation of mixtures of amphoteric substances

(3) Separation of uncharged molecules in the form of charged complexes

C. *Investigation of the nature and stability of ionic species in solution*

applications, use is made of the ion-exchange properties of the resin. In addition, ion-exchange resins may be used in the process known as 'ion-exclusion'¹, in partition chromato-

graphy², in 'salting-out' chromatography³, and as catalysts in many chemical reactions⁴; in these applications, use is made of other properties of ion-exchange resins, e.g. the absorption of non-electrolytes and the exclusion of strong electrolytes.

It will be seen from *Table 7* that the more important laboratory applications can be divided into three groups: the first group consists of applications which involve merely the replacement of ions in solution by ions from the resin; the second consists of applications in which use is made of ion-exchange chromatography; and in the third group ion-exchange resins are used to study the nature of ionic species in solution. A short description of the general techniques and apparatus used in these applications is given below. The different procedures are described in more detail in the following chapters, which include experiments illustrating the more important applications.

Replacement of Ions

In simple procedures which merely involve the replacement of ions in the solution by ions from the resin, elaborate apparatus is not required, a column procedure almost invariably being employed, except in cases when ion-exchange reactions are carried out with difficultly soluble substances, or when only a limited degree of exchange is required as, for example, when ion exchange is used to adjust the pH of a solution. Simple columns of the type shown in *Figure 22(a)* are suitable for most laboratory applications. The bed of resin is contained in a glass tube and is supported on a plug of glass wool or on a sintered glass disc. For experiments on a very small scale, a pipette containing a small glass wool plug may be used as a column. If a large column is in continual use, inlets can be provided for regenerants and wash water, and provision made for backwashing. Arrangements of this kind, however, are unnecessary and undesirable in the small columns used in analytical work. Strongly acidic and strongly basic resins are usually employed, those based on cross-linked polystyrene generally being the most suitable. The preparation of the resins for use is described in Chapter 6 and some typical laboratory applications are described in Chapters 8 and 9.

The uses of replacement procedures in preparative work and for the de-ionization of water are described in Chapter 10.

Separation of Mixtures of Ions

As has been seen in Chapter 4, three procedures may be used for the separation of mixtures of ions by ion-exchange chromatography; in all these methods a column of resin is used, and solutions are passed downwards through the resin bed. To obtain satisfactory separations, it is essential that the solutions should pass through the column in a uniform manner. The resin particles should be packed uniformly in the column, and the resin bed should be free from air bubbles, so that there is no 'channelling' and no undue disturbance of the band boundaries. A column of the type shown in *Figure 22(b)* is suitable for most chromatographic experiments. It is an advantage if the tap funnel or aspirator which is used as a reservoir is connected to the column with a short length of rubber or PVC tubing; the flow rate of solutions can then be easily adjusted by raising or lowering the reservoir. The ratio of the height of the column to its diameter is not very critical, a ratio of about 10 or 20:1 usually being employed but ratios of 100:1 have been used. In displacement development procedures where the boundaries are self-sharpening (*see* Chapter 4), a series of columns of decreasing diameter [*Figure 22(c)*] are sometimes used. A boundary which has become distorted as a result of channelling in one column, will be reformed in the following column, but if this column is of a smaller diameter, then the effect of any further distortion of the boundary will be correspondingly less. This arrangement of columns in series should not be used in elution chromatography, however.

As mentioned in Chapter 4, the technique known as gradient elution is sometimes employed in elution chromatography instead of using a series of eluting agents; in this procedure, the composition of the eluting agent is changed gradually and continuously. In the usual method of carrying out gradient elution, a small reservoir containing an eluting agent of the desired initial composition is connected to the top of the column. As this eluting agent passes into the

INTRODUCTION

column, the contents of the reservoir are stirred (usually with a magnetic stirrer) and, at the same time, an eluting agent of

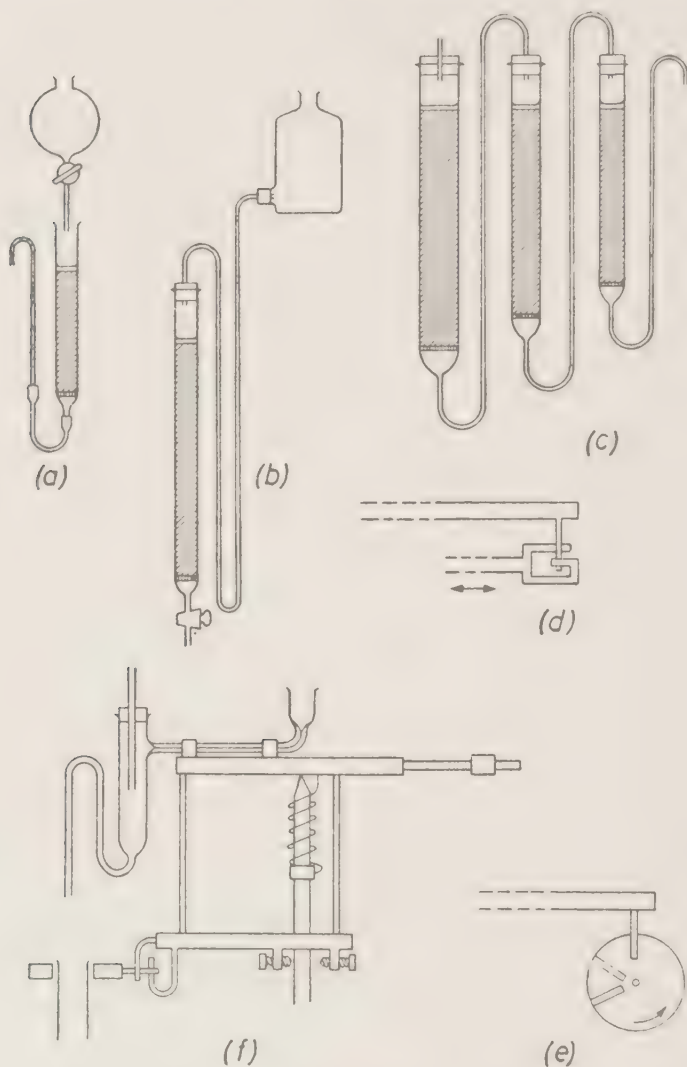


Figure 22. Ion-exchange apparatus: (a) column for simple replacement procedures; (b) column for ion-exchange chromatography; (c) coupled columns for use in displacement development; (d) and (e) escapement devices for fraction cutters; (f) constant-volume fraction cutter

the desired final composition is added to the reservoir. In this way the composition of the eluting agent passing through the column can be changed steadily and continuously.

Whichever chromatographic procedure is adopted, the effluent from the column has, usually, to be collected in fractions. These are then individually analysed and, in preparative work, the constituents of the mixture are isolated from the appropriate fractions of the effluent. The fractions, which are usually of equal volume, may be collected manually but, in a lengthy experiment, this can be very tedious and an important fraction can easily be lost. If, therefore, a number of chromatographic experiments have to be carried out, the use of an automatic fraction cutter is a great advantage. Several different types are commercially available, but simple and reliable fraction cutters can be fairly easily constructed in the laboratory. The most suitable type will depend on the particular application, but a fraction collector which will collect from 20 to 50 fractions, each with a volume of from 5 to 25 ml., could be used satisfactorily in most chromatographic experiments. In the majority of laboratory fraction cutters, the effluent from the column is collected in test tubes, on either a time basis or a volume basis. The test tubes, which receive the effluent, are usually placed in a circular rack and the receiver is changed either at fixed time intervals, or when a predetermined volume of the effluent has been collected.

Fraction cutters operating on a time basis are probably most easily constructed and, if the flow rate of the solutions through the column is constant, the fractions will be of equal volume. In the simpler types, the test tubes are mounted around the periphery of a turntable, the motive power for the rotation of which can be provided either by a clockspring or by a weight attached to a light cord which passes over a pulley and is then wound round the spindle of the turntable. Small pins, one for each receiver, are fixed near the periphery of the turntable so that its movement can be controlled by an escapement mechanism. Two simple escapement devices are shown in *Figure 22(d)* and *(e)*. In the first⁵, the gate of the escapement is moved momentarily, by a solenoid or an electromagnet, in the direction indicated and is then returned to its original position. This movement allows one of the pins on the turntable to pass through the gate of the escapement, the turntable rotates, and another receiver is brought into

INTRODUCTION

position under the outlet from the column. The necessary electrical impulses for the operation of the solenoid or electromagnet can be provided by a suitable time switch. In the second type of escapement [*Figure 22(e)*] the gate is formed by radial slots cut in two discs which are mounted a short distance apart on a common shaft; the latter is driven at a constant speed by a small electric or clockwork motor⁶.

A method of construction which can be used for a simple type of constant-volume fraction cutter is shown in *Figure 22(f)*⁷. The effluent from the column is collected in the central funnel and then passes through a length of 1 mm bore capillary tubing to the syphon tube from which it is transferred to the receivers in fractions of equal volume. In this cutter, the receivers, which are stationary, are held in a circular rack and the syphon tube moves in a circle over the receivers. As shown in the diagram, the beam carrying the syphon tube is mounted on a central pivot; a torque is applied to the beam by a helical spring but the rotation of the beam is controlled by an escapement mechanism operated by the changes in weight of the syphon tube. The volume of liquid delivered by the syphon can be varied by raising or lowering the central tube.

If coloured bands are formed in the column, the progress of a chromatographic separation can be followed visually. Usually, however, it is necessary to analyse the effluent in order to determine the degree of separation which has been achieved. Chemical tests are often used but physical methods, e.g. the determination of electrical conductivity or ultra-violet absorption, are frequently more convenient. In elution chromatography, if the changes in concentration of the ions being separated can be determined, then the degree of cross-contamination and the purity of the isolated constituents can be estimated.

Some difficulty is often encountered in selecting a suitable ion-exchange procedure for the separation of a given mixture. As we have seen, either frontal analysis, displacement development, or elution may be used. The latter procedure is usually the most suitable since, under favourable conditions, complete separations can be achieved. Most inorganic

separations are now carried out under conditions such that complexes are formed; in this way the separation factor can be very greatly increased. Where the use of a complexing agent is unnecessary, the separation can often be achieved more simply by methods other than ion-exchange chromatography. One exception to this generalization, however, is the separation of the alkali metals which can be achieved using hydrochloric acid as the eluting agent. Mixtures of inorganic cations can be separated by two general methods:

- (1) The cations are absorbed on a column of a cation-exchange resin (which is usually in the hydrogen or ammonium form) and the column is then eluted with a solution containing a complexing agent such as citric acid, ethylenediaminetetraacetic acid or phosphoric acid (*see* Chapter 10).
- (2) An anion-exchange column is used. The constituents of the mixture, even if normally in the form of cations, are separated in the form of anionic complexes, e.g. as negatively charged chloro-complexes or as complex cyanides. The elegant procedures devised by Kraus and Nelson⁸ which are of very wide application, depend on the formation of chloro-complexes. The differences in stability of these complexes are often such that difficult separations can be readily achieved simply by using a strongly basic resin in the chloride form and hydrochloric acid solutions as eluting agents.

The separation of organic ions is often based on differences in the degree of dissociation of the components in the mixture. For example, organic bases can be separated by elution using a column of a strongly acidic resin in the hydrogen form. The mixture of bases is absorbed on the column which is then eluted with acid or, if more precise control over the pH is required, a buffer solution can be used. Under these conditions the stronger bases will be more readily absorbed and the weaker bases will appear first in the effluent.

As might be expected, either cation-exchange or anion-exchange chromatography can be used for the separation of complex mixtures of amphoteric ions such as amino acids or

INTRODUCTION

peptides. The procedures are similar in principle to those which would be used for the separation of mixtures of organic bases or organic acids and usually depend on the differences in the degree of dissociation of either the acidic or basic groups. For further details of these methods, which are of great value for the separation of complex mixtures of biochemical origin, the reader is referred to a textbook on the applications of ion exchangers in organic chemistry and biochemistry⁹.

Occasionally mixtures of uncharged substances can be separated in the form of charged complexes by ion-exchange chromatography. For example, sugars can be separated in the form of their borate complexes, and aldehydes and ketones can be separated in the form of their bisulphite compounds.

Investigation of Ionic Species in Solution

In the study of complexes, batch experiments are usually employed, i.e. the resin is shaken with the solution until equilibrium is attained; in some cases, however, considerable information can be obtained from column experiments. Details of the procedures used are given in Chapter 11.

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Chapter 6

BASIC EXPERIMENTS WITH CATION- AND ANION-EXCHANGE RESINS

Introduction

THE experiments given in this chapter are designed to illustrate points of fundamental importance in the application of the ion-exchange process. For this reason we have not hesitated to include as an experiment the pretreatment of the resin prior to use, for not only is it essential for many purposes to have the resin purely in one form, but this experiment illustrates a number of the features peculiar to the use of resins. The other experiments are concerned with resin capacity, the equivalence of exchange, the extent to which exchange proceeds under equilibrium conditions, and some factors controlling rate of exchange. An understanding of the role each of these may play in the ion-exchange process is essential not only for the experiments described in the later chapters, but also for any successful application of ion exchange.

A number of important points are discussed both in the descriptions of the experiments and the notes at the end of each experiment. Since these are not always repeated in later chapters it is recommended to the research chemist (who may feel that he needs no practice with these simpler experiments) that he read this chapter first before proceeding to try the experiments in the later chapters, or to adapt them to his own purposes.

The experiments described in this chapter, and in the following one, are particularly suitable for sixth form pupils or first and second year university students to perform, and in order to enable them to complete the longer experiments, which may extend over more than one period of practical work, the points at which experiments may be left have been indicated in the text by an asterisk. Where this involves

EXPERIMENTS

leaving solutions running through a column it is essential to see that the receiver is large enough to accommodate all the liquid which will pass through. With the needs of the schools

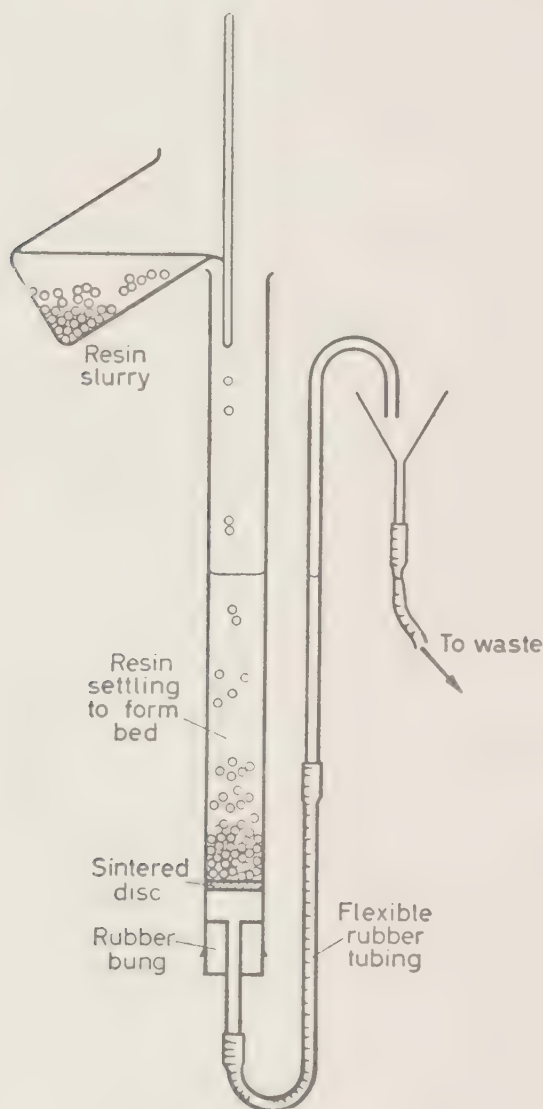


Figure 23. Filling an ion-exchange column

in mind, we have suggested volumetric methods of analysis wherever this is possible, but in Experiment 4(b) there is no convenient alternative to the gravimetric determination of sulphate. As a result, this experiment may be thought less

suitable for schools, who for reasons of cost may also prefer to modify Experiment 4(a) by omitting the determination of the capacity for silver ions. However, in this latter case a comparison of the equivalence of exchange $\text{H}^+ \dots \text{Cu}^{++} \dots \text{Na}^+$ is sufficient to illustrate the point.

Experiment 1. Preliminary Treatment of the Resins^a

(a) *Preparation of the Air-dried Hydrogen Form of a Strongly Acidic Cation Exchanger*

Shake 1 lb. of the resin (either 'hydrogen' or 'sodium' form as supplied, preferably 50–100 mesh) slowly and stir into 1 l. of water in a 3 l. beaker, adding more water if the slurry becomes too thick^b. As the resin settles after stirring is stopped, it will sometimes be found that the supernatant liquid is turbid. If so, it should be poured off and the resin washed several times by decantation. Occasionally a few large beads float on the water and are lost on decantation—they are of no use and may be rejected safely.

Next, decant the slurry into a large column (*Figure 23*) (60 cm × 4.5 cm) which has been half filled with water (all the air must be displaced from below the sintered glass disc or supporting glass wool pads before addition of the slurry). The resin settles and forms a bed, supported on the disc or glass wool pads. During this process any surplus water drains off through the overflow, but care should be taken that at no stage does the level of the water fall below the top of the resin bed, otherwise bubbles will be trapped in it^c.

Wash the column briefly by an upward flow of water of sufficient velocity to cause the resin bed to become fluid. The water is led from the top of the column through a tube carried in a rubber bung, into a trap, and thence to waste (*Figure 24*). If any large bulk of resin is washed over by accident it may be recovered from the trap, but small quantities of very fine resin or of very light beads are usually rejected. When the bed has been thoroughly agitated, gradually decrease the velocity of the water stream so that the resin settles slowly to give a bed of uniform packing. Once the bed has settled, apply a pinch-clip to the rubber tube connecting the column to the side tube before removing

EXPERIMENTS

the rubber bung and disconnecting the distilled water feed. In this way the possibility that the water in the column will drain below the level of the top of the resin bed will be avoided.

Adjust the height of liquid in the column, by altering the height of the side arm, to just above the level of the resin and maintain this whilst passing 2 N HCl through the column in a downward direction (*Figure 25*). If the resin was initially in the sodium form it will be necessary to pass the acid solution through the column until the effluent is free from sodium ions

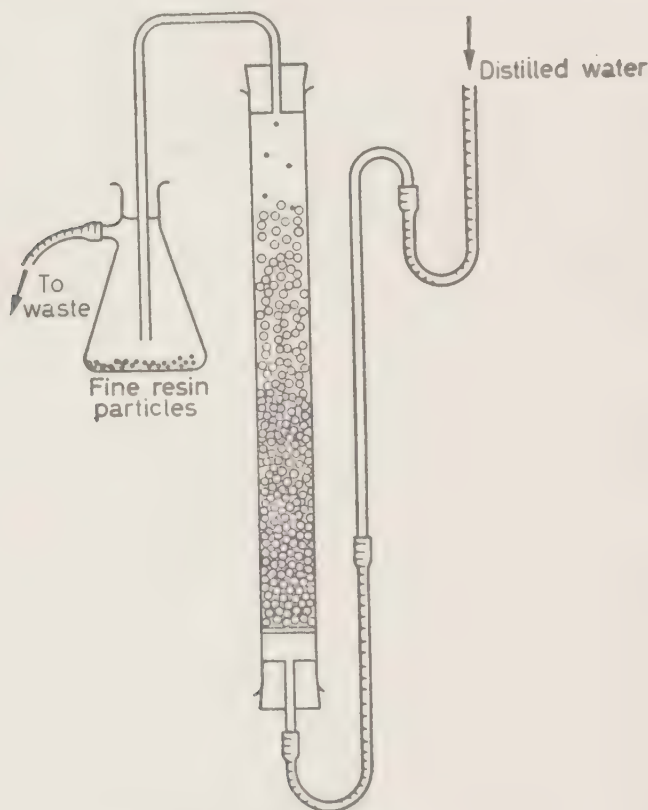


Figure 24. Backwashing the column

and the concentration of acid in influent and effluent is identical; then pass a further 1–2 l. of acid to ensure complete conversion to the hydrogen form. If the resin was already in the hydrogen form some 2 l. of acid should be passed through the column to ensure removal of any metallic impurities sorbed on it. The rate of flow should be approximately 2 l./h.

Whilst still maintaining the liquid level, wash the column with water by downward flow until the effluent is free from chloride ions or acid^{d*}. Slowly invert the column over a 3 l. beaker and with a gentle flow of water wash the resin into a beaker and then filter off the resin on a Büchner funnel. Wash the resin on the filter once or twice and then remove as much water as possible by suction.

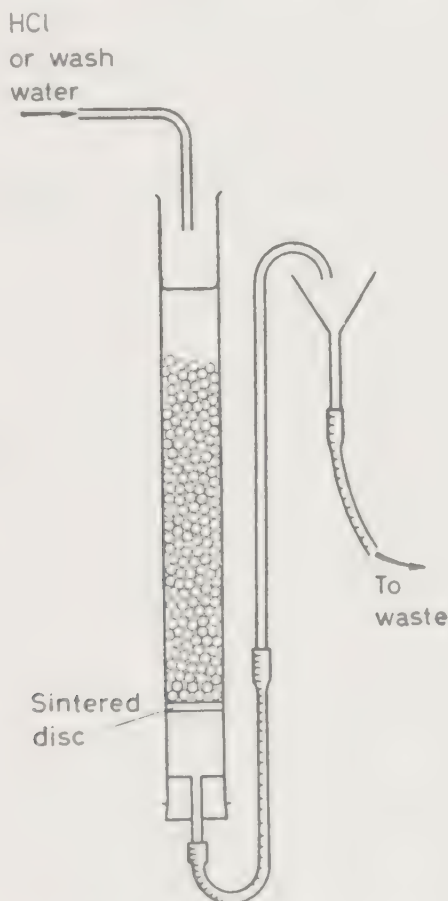


Figure 25. Treatment of resin

Transfer the resin to a large evaporating basin, cover lightly to protect it from dust whilst giving access to the air, and leave in a warm place (25–30°C, not higher) until the resin is completely free running, i.e. 2–3 days^e. If a graded resin was not used, separate the beads into 20–50, 50–100, and 100–200 mesh fractions by means of clean sieves; these will provide stock resins for the experiments which follow.

EXPERIMENTS

(b) *Preparation of the Air-dried Chloride Form of a Strongly Basic Anion Exchanger*

The resins of this type are usually supplied in the chloride or hydroxide form^f and the treatment required is the same as that described in Experiment 1(a)^g. If the resin is initially in the hydroxide form it should be stirred first with 2 N HCl to remove carbonate before further treatment in the column to ensure complete conversion of the resin to the chloride form. With the resin initially in the chloride form, the passage of some 2 l. of acid through the column should be adequate^h.

Notes

- ^a It is advisable that even analytical grade resins should be given this treatment. The description 'analytical grade', when applied to resins, indicates that every care has been taken in their preparation and that they are, as near as possible, in the form indicated on the label. However, the nature of the resins is such that they very readily pick up foreign ions—polyvalent ones in particular (e.g. Fe^{3+} by the cation exchangers) in the process of washing—by ion exchange.
- ^b Unless it is very damp when supplied, the resin will sorb water and swell when poured into it; this swelling is particularly marked with resins of a low degree of cross-linking. It is inadvisable to pour dry resin into a glass column and to add the water afterwards, for, very often, the column will be shattered by the expansion—hence the method described here for preparing a slurry is preferable.
- ^c Air bubbles trapped between the resin beads will prevent both the reagents used to treat the resin and the wash water from coming into complete contact with all the beads, and treatment of the resin will therefore be uneven.
- ^d The water used for washing must be good quality distilled or de-ionized water (see Chapter 9), otherwise the resin will again pick up cationic impurities from the water.
- ^e Since the resin contracts on drying and swells again on wetting (processes which, if repeated too often and under too drastic conditions, may cause fracture of the beads) it is not recommended to dry it at high temperatures (e.g. 100°C). The authors' experience is that drying in the air produces a material, which although of higher water content, is free running and easy to handle and will swell less in water. The capacity of this resin has been found to remain constant (despite variations in relative humidity of the air) over a long period, if kept in a closed bottle.
- ^f Where the analytical grade resin is supplied in the hydroxide form it may be kept for experiments requiring the resin in this form, when it is best used without prior treatment unless the presence of carbonate is objectionable.
- ^g Hydrochloric acid is used for treatment of both cation- and anion-exchangers, but in the first case it is the hydrogen ions of the acid which are exchanged and in the second case the chloride ions.
- ^h If the anion-exchange resin is washed with ordinary distilled water then it may prove difficult to obtain washings which are completely free from chloride—probably because carbonic acid in the water tends to displace chloride ions from the resin under the non-equilibrium conditions of column operation. It is generally satisfactory to stop washing once the washings give no more than a slight turbidity with silver nitrate.

Experiment 2. Determination of the Capacity of a Resin by a Batch Method and Some Experiments on Extent and Rate of Exchange

(a) *The Capacity of a Cation-exchange Resin*

To 0.5 g^a of air-dried, hydrogen form cation-exchange resin (if sieved, use 50–100 mesh fraction) in a 250 ml. conical flask add 50 ml. of 1 M sodium chloride solution^b and one or two drops of phenolphthalein indicator. Swirl the flask gently and titrate the contents slowly with standard sodium hydroxide solution (approximately decinormal). The approach to the end point should be made very slowly^{c,d}.

Now the reaction which is taking place may be represented as:



(where barred formulae refer throughout to ions present in the resin phase) and, since excess of sodium chloride is present and since the acid liberated is neutralized in the titration, it proceeds to completion. Thus the volume of standard alkali required to produce a permanent pink coloration in the indicator is equivalent to the hydrogen ions initially present in the resin phase.

Hence, if the volume of sodium hydroxide solution (normality = x) used is v ml., then the resin is equivalent to $xv/1,000$ equivalents (i.e. xv milliequivalents) of NaOH. Now if the mass of resin used was m g, then 1 g of resin is equivalent to xv/m milliequivalents; i.e. its capacity for hydrogen (or other cations) is xv/m millicquivs./g, since that number of milliequivalents of hydrogen ions were initially present in 1 g of the resin phase^e (air-dried state). (If $m=0.5$ g and $x=0.1$ then the capacity in millicquivs./g is given numerically by $v/5$).

(b) *The Capacity of an Anion-exchange Resin*

The capacity of the chloride form resin prepared in Experiment 1(b) is less conveniently determined by a batch method, but if a sample of the hydroxide form of a strongly basic anion exchanger is available then the following experiment may be performed.

EXPERIMENTS

To 1 g^a of hydroxide form anion-exchange resin (as received) in a 250 ml. conical flask, add 50 ml. of 1 M sodium chloride solution^b and two or three drops of methyl orange indicator. Swirl the flask gently and titrate the contents slowly with standard hydrochloric acid solution (approximately decinormal). As the end point is approached, stop the titration, heat the flask and contents to 80–90°C for 2–3 minutes, cool to room temperature and complete the titration, but proceed very slowly near the end point^c.

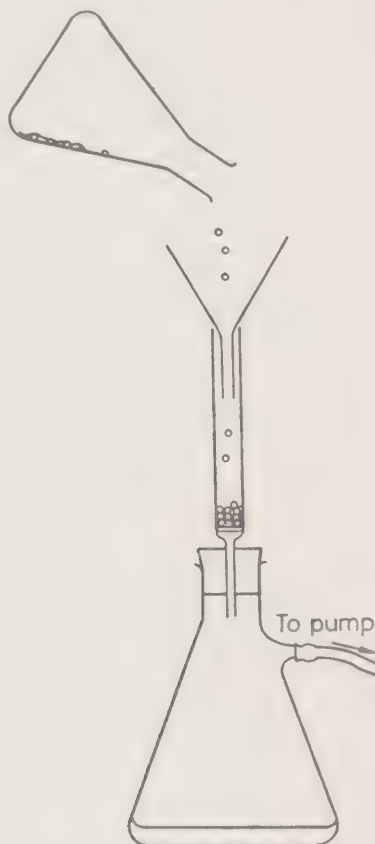


Figure 26. Transfer of resin to column

The reaction which occurs may be represented



but it is driven to completion both by the presence of excess sodium chloride and by the neutralization of the alkali liberated in the titration.

As in Experiment 2(a) the capacity of the resin is given by ve/m millicquivs./g, where v ml. is the volume of y N hydrochloric acid required to neutralize the alkali liberated^{e,f}. If $m=1$ g and $y=0.1$ then the capacity is given numerically by $v/10^e$.

Filter the suspension of resin in the flask through a 3 in. funnel into a small column (10 cm \times 1 cm) using suction (see Figure 26) and by means of a jet of water from a wash bottle transfer the resin completely to the column. By means of a rubber tube, connect the column to a side tube [see Figure

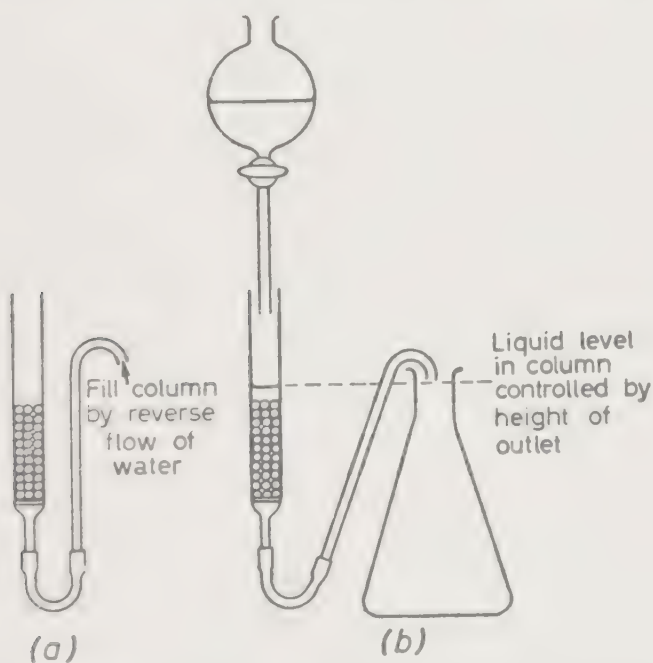


Figure 27. (a) Filling the column with water;
(b) column in operation

27(a)]. Connect the outlet of this tube to a wash bottle (or aspirator containing water) by means of a short rubber tube and fill the column with water by an upward flow, taking care to displace any air from beneath the disc. Disconnect the wash bottle or aspirator and wash the resin by a downward flow of water at a rate of flow not exceeding 100 ml./h [Figure 27(b)]. Under these conditions 750 ml. to 1 l. of water should be sufficient to reduce the chloride ion concentration in

EXPERIMENTS

the washing to a mere trace^{s*}. The capacity of the resin, which is now in the chloride form (see equation on p. 80), may be determined by the method given in Experiment 3(b), as a check on the result obtained in the method given above.

(c) *An Equilibrium Experiment*

To 0.5 g^a of air-dried, hydrogen form cation-exchange resin [use material from the same batch as that used for Experiment 2(a)] in a 250 ml. conical flask add exactly v ml. of x M sodium chloride solution [where v and x have the same values as in Experiment 2(a)] and $(50-v)$ ml. of distilled water (both should be added from a burette). Stopper the flask firmly with a clean rubber bung and leave the contents to stand, with occasional swirling, for at least five hours (if mechanical shaking is employed the time may be reduced to one hour)*.

Filter the solution through a dry 'fast-filtering' paper into a dry 250 ml. conical flask^d. Titrate a 25 ml. portion of the filtrate with standard sodium hydroxide solution (approximately decinormal) and hence calculate the number of milliequivalents of acid present in the 50 ml. of solution^h. From this value, and from the value of the capacity of resin already determined [Experiment 2(a)] calculate, as a per cent value, the extent to which the reaction



proceeds toward completion when equivalent quantities of H^+ and Na^+ ions are present in the system. It will be found that with a strongly acidic cation-exchange resin the reaction will have proceeded beyond halfway in the left in right reaction indicating that the affinity of sodium ions for the resin is greater than that of hydrogen ions for the resin.

(d) *A Study in Rate of Exchange*

Repeat Experiment 2(a) but with the following modifications:

1. Use exactly 50 ml. of 0.05 M NaCl and place this first in the flask.
2. Next, add 1 ml. of the standard sodium hydroxide solution.

3. Finally, add the resin, at the same time starting a stop watch. As soon as the colour of the phenolphthalein indicator is discharged note the time and add a further 1 ml. and so on. Plot time in seconds against volume of standard NaOH added.

Repeat the experiment with (i) 0.01 M NaCl (ii) 0.005 M and (iii) 0.002 M NaCl, in place of the 0.05 M NaCl used first^d.

It will be evident from the results obtained (see *Figure 28* for some typical results) and from Experiment 2(a) that the rate at which the hydrogen ions in the resin phase are exchanged for sodium ions from the solution is only rapid when the sodium ion concentration in the solution is high (repetition of these experiments with 0.05 M, 0.01 M, 0.005 M

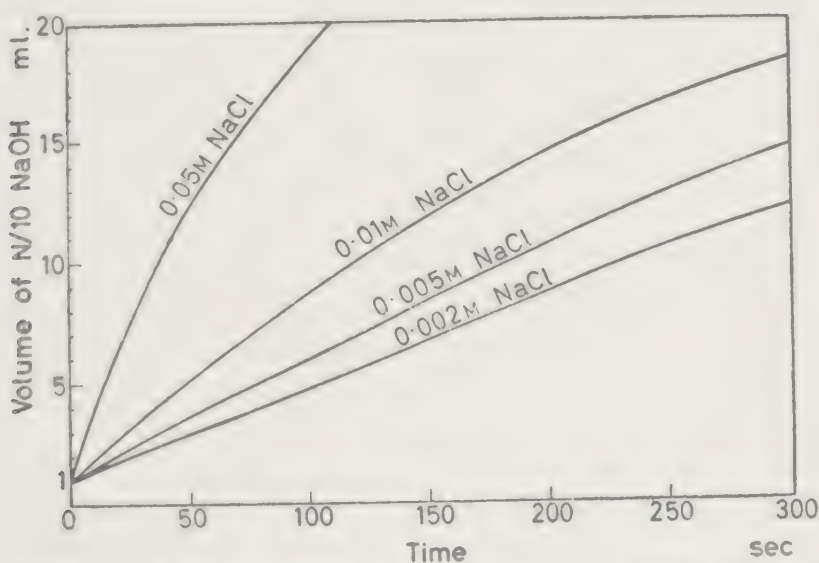


Figure 28. Rate of addition of 1 ml. portions of N/10 NaOH to maintain an alkaline reaction to phenolphthalein indicator in an aqueous suspension (50 ml. liquid volume) of 0.5 g hydrogen from cation exchanger in the presence of NaCl at 20–25 °C

and 0.002 M NaNO₃ will provide sufficient indication that it is the concentration of sodium ions which is important). The reason for a low rate of exchange with a low concentration of sodium ions in solution is that under these conditions the film of solution immediately in contact with the resin beads is rapidly depleted of sodium ions by exchange with hydrogen ions from the resin and hence further exchange is delayed until more sodium ions from the bulk solution can diffuse

EXPERIMENTS

into this surface film. With a higher concentration of sodium ions in the bulk solution such diffusion will occur more readily and the exchange will proceed more rapidly.

Evidently under the conditions of these experiments the rate-determining step in the exchange process is that of 'film diffusion' (see Chapter 3, p. 46).

Notes

- ^a It is possible to use an accurately known mass of resin between 0.4 and 0.6 g for the cation-exchange experiments or between 0.8 and 1.2 g for the anion-exchange experiments. However, if an air damped balance is available then it is convenient to weigh out exactly 0.5 or 1 g (± 0.0005 g) onto a tared aluminium scoop. The transfer of beads on or off the scoop is easily controlled by a small camel-hair brush and the resin is likewise readily transferred to the flask.
- ^b Neither the volume nor the strength of the sodium chloride solution need be known accurately. It is possible to use 50 ml. water and to add solid sodium chloride (N.B. analytical grade reagents should be employed in all the experiments described), but it is necessary to have a large excess of sodium chloride present (i.e. *ca.* 50 millimoles for 3–5 milliequivs. resin) otherwise the rate of exchange will be slow [cf. Experiment 2(d)] and a false end point may be obtained in the titration.
- ^c Ion-exchange reactions, although ionic reactions, are not instantaneous; the rate of exchange may be determined by the rate of diffusion of ions within the resin phase (particle diffusion) or by the rate of diffusion of ions across the resin particle-solution boundary (film diffusion). It is therefore necessary to allow time for the exchange process to be completed.
- ^d The resin may be saved for regeneration and re-use. Resins of each type (cationic and anionic) are of course kept separately, but in addition it may be convenient to keep the different mesh sizes of each type apart. When sufficient of any one group of 'residues' has been accumulated it may be regenerated by the methods given in Experiment 1(a) or (b), but great care must be taken to use sufficient regenerant as some ions are very firmly bound to the resin (e.g. dichromate ions are not readily displaced from an anion exchanger by hydrochloric acid). In some cases alternative regenerants may be desirable.
- ^e With air-dried cation-exchange resins a capacity of 3.6–4 milliequivs./g are often found whilst, with anion-exchange resins, values of the order of 3 milliequivs./g might be expected (lower values may be found for moist hydroxide form resins). Higher values which are sometimes quoted generally refer to oven-dried (100°C) resins (see Note ^e Experiment 1). Duplicate measurements on the same batch of resin should give values differing by not more than 1 part in 300 and provided that the resin is allowed sufficient time to dry in the first place and is afterwards kept in a stoppered bottle the capacity should not vary appreciably with time. For the accurate determination of anion-exchange capacities, the method given in Experiment 3(b) is to be preferred to that in Experiment 2(b).
- ^f If the given procedure is followed, any carbonate present in the resin phase should also be displaced by chloride, and the sodium carbonate thus liberated,



will be titrated; hence the total capacity should be recorded, regardless of the presence of carbonate.

^a See Experiment 1, Note *b*. This procedure will cause hydrolysis (and consequent loss) of chloride from any sites of weakly basic character which are inevitably present to the extent of a few per cent even with a modern strongly basic resin. Hence only the 'strong base' capacity will be measured by the method given. The full capacity could be obtained by the use of N/1,000 HCl in place of water for washing. This should be passed until the chloride content of the effluent is the same as that of the influent. The hydrochloric acid present in the liquid then remaining in the column will not appreciably affect the accuracy of the subsequent determination of capacity.

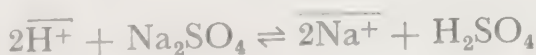
^b In this experiment the fact that the dry resin will absorb some water and hence cause a slight change in the volume of the solution may be ignored.

Experiment 3, Part 1. Determination of the Capacity of a Resin by a Column Method

(a) *The Capacity of a Cation-exchange Resin*

Partly fill a small column (10 cm × 1 cm) [Figure 27(a)] with water, taking care to displace any air from beneath the sintered glass disc. Weigh out 0.5 g^a of air-dried cation-exchange resin (50–100 mesh fraction) on an aluminium scoop and transfer it with the aid of a small brush through a dry 3 in. funnel into the column. Add sufficient water to cover the resin. If air bubbles stick to any of the resin beads they must be dislodged; this is generally achieved by applying an intermittent pressure to the rubber tubing, thus causing the liquid to rise and fall a little in the column. Adjust the level of the outlet tube so that the liquid in the column will drain to a level just above the resin beads.

Fill a 250 ml. tap funnel with a solution (approximately M/4) of sodium sulphate and allow this to drip into the column at a rate of about 100 ml./h^b and collect the effluent in a conical flask (500 ml. capacity) [Figure 27(b)]*. When all the solution has passed into the column, titrate the effluent with standard (approximately decinormal) sodium hydroxide. Now the reaction may be represented:



[cf. Experiment 2(a)], but the reaction proceeds to completion since not only is an excess of sodium sulphate employed, but any acid liberated is swept out of the column by the flow of solution through the column.

EXPERIMENTS

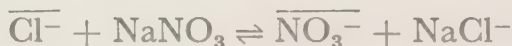
As in Experiment 2(a) the capacity of the resin in milliequivalents/g will be given by xv/m , where v ml. of x N NaOH are required to neutralize the acid liberated from m g of resin^c. (If $x=0.1$ and $m=0.5$ then the capacity is given numerically by $v/5$.)

(b) *The Capacity of an Anion-exchange Resin*

Introduce 1 g^a of the air-dried, chloride form of a strongly basic anion exchanger [Experiment 1(b), 50–100 mesh fraction] into a small column partly filled with water, according to the method described in Experiment 3(a).

Fill a 250 ml. tap funnel with a solution (approximately M/4) of sodium nitrate and allow this to drip into the column at a rate of 100 ml./h^b*. Collect the effluent in a 500 ml. conical flask and titrate with standard silver nitrate solution (approximately N/10) using potassium chromate indicator solution.

As in Experiment 3(a) the reaction which occurs, in this case,



is again driven to completion and the chloride ions initially in the resin phase are completely displaced and appear in the effluent. If v ml. of y N AgNO₃ are required in the titration of the effluent from a column containing m g of resin then the capacity of the resin is yv/m milliequivalents/g^c. (If $m=1$ and $y=0.1$ then the capacity is given numerically by $v/10$.)

Experiment 3, Part 2. Studies in the Conversion of Resins from One Form to Another

(c) *Conversion of a Cation Exchanger*

Repeat Experiment 3(a), but use 2 g of resin and change the receiver after each 25 ml. of effluent has been collected (e.g. use a measuring cylinder as the receiver and transfer the effluent to a conical flask before titration). Titrate each fraction separately with standard sodium hydroxide solution (approximately N/20). Plot a graph of total milliequivalents of acid liberated against volume of liquid passed through the column^d.

(d) *Conversion of an Anion Exchanger*

Repeat Experiment 3(b), but use 2 g of resin and change the receiver after each 25 ml. of effluent has been collected, as in Experiment 3(c). Titrate each fraction separately with standard silver nitrate solution (approximately N/20). Plot a graph of total milliequivalents of chloride liberated against volume of liquid passed through the column^d.

Notes

^a See Experiment 2, Note *a*.

^b See Experiment 2(d), from which the need to allow sufficient time of contact between solution and resin should be apparent. In these experiments it is not strictly necessary for the solution to be in equilibrium with the resin with which it is in contact at any given time, but unless time is allowed for the exchange to proceed to a significant extent then a vast bulk of solution will be required to liberate all the hydrogen ions from the cation exchanger or all the chloride ions from the anion exchanger.

^c See Experiment 2, Notes *d* and *e*.

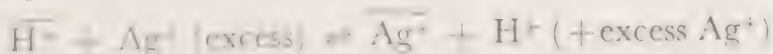
^d Even with the larger quantities of resin in Experiments 2(c) and (d) 250 ml. of Na₂SO₄ and NaNO₃ solutions respectively should be adequate to convert the resins completely to Na⁺ or NO₃⁻ forms. A check is thus provided that the quantities of solution specified in Experiments 2(a) and (b) are adequate.

Experiment 4. Determination of Equivalence of Exchange

(a) *Cation-exchange Experiments*

Partly fill a column (15 cm × 1.5 cm) [Figure 27(a)] with water, taking care to displace any air from beneath the sintered glass disc. Introduce 3 g air-dried cation-exchange resin (hydrogen form 50–100 mesh) into the column through a dry 3 in. funnel and add sufficient water to cover the resin. Dislodge any air bubbles adhering to the resin beads [see Experiment 3(a)] and adjust the level of the outlet tube [Figure 27(b)] so that the resin beads are just below the liquid level.

Fill a 250 ml. tap funnel with 0.1 M silver nitrate solution, allow this to drip slowly into the column at a rate of about 100 ml./h* and collect the effluent for silver residues. When all the solution has passed through the column the resin should be completely in the silver form.



Since the tap funnel thoroughly, fill it with water and allow this to drip through the column at about 100 ml./h. When

EXPERIMENTS

the funnel is empty, refill it and repeat the process until the washings give a very faint precipitate only when treated with a solution of a chloride (probably 3×250 ml. water will be needed). Next elute the silver ions sorbed on the column by the slow passage (100 ml./h) of 250 ml. of 2 M nitric acid through the column and collect the effluent in a 500 ml. graduated flask*. Finally, wash the column with water so that the combined effluent and washings are just less than 500 ml.* Mix the contents of the flask thoroughly and dilute to the graduation mark. Use a 50 ml. aliquot of this solution to determine the amount of silver present (e.g. volumetrically by Volhard's method or gravimetrically as silver chloride) and hence find the amount of silver sorbed on the resin. Calculate the capacity of the resin for silver ions.

Continue washing the column until the washings are neutral to methyl orange*. Fill the tap funnel (250 ml.) with 0.1 M copper sulphate solution and allow this to drip into the column at the same rate of 100 ml./h. Rinse the funnel thoroughly with water and wash the column as before until free from electrolyte (test for sulphate with barium chloride solution)*. Elute the copper with 250 ml. 2 N nitric acid passed at the rate of 100 ml./h through the column and follow this with not more than 250 ml. of water. Collect the eluate and washings in a 500 ml. graduated flask, mix thoroughly and dilute to the mark. Use a 50 ml. aliquot for the determination of the copper present in the eluate (e.g. by titration with standard sodium thiosulphate solution) and calculate the capacity of the resin for Cu^{++} ions.

Once more continue washing the column until the washings are free from acid^{a*}. Determine the capacity of the resin for hydrogen ions by the method given in Experiment 3(a), but use just less than 500 ml. of the approximately M/4 sodium sulphate solution and collect the effluent in a 500 ml. graduated flask. Dilute the effluent to 500 ml. and use an aliquot portion for the determination of the acid present.

Calculate the capacity of the resin for hydrogen ions and compare the results with those found for silver and cupric ions^{b,c}.

(b) Anion-exchange Experiments

Partly fill a column (15 cm \times 1.5 cm) [Figure 27(a)] with water, taking care to displace any air from beneath the sintered glass disc. Introduce 4 g air-dried anion-exchange resin (chloride form, 50–100 mesh) into the column through a dry 3 in. funnel, add sufficient water to cover the resin, dislodge any air bubbles from the resin beads [see Experiment 3(a)] and adjust the level of the outlet tube [Figure 27(b), also Experiment 4(a)].

Fill a 250 ml. tap funnel with 2 M nitric acid and allow this to drip through the column at a rate not exceeding 100 ml./h, follow this with just less than 250 ml. of water*, and collect effluent and washings in a 500 ml. graduated flask. Mix the contents of the flask thoroughly and dilute to volume. Use a 50 ml. aliquot for the determination of the chloride present in the effluent and hence present initially on the resin.

Repeat the procedure using first a nearly saturated sodium sulphate solution (250 ml., followed by just less than 250 ml. water), which will convert the resin to the sulphate form and liberate the nitrate absorbed^d, and secondly 2 M hydrochloric acid (250 ml., followed by just less than 250 ml. water) which will liberate the sulphate sorbed and convert the resin to the chloride form once more. In the second case, a gravimetric estimation of the sulphate content of an aliquot portion of the combined effluent and washings (dilute to 500 ml. for convenience) will enable the sulphate present on the resin to be determined.

Compare the capacity of the resin for chloride and sulphate ions ^{b,c}.

Notes

* If desired, the capacity towards a trivalent ion may be determined by loading the column by passage of 250 ml. of, for example, a solution (pH 1–2) of ferric sulphate in very dilute sulphuric acid, through the column; such a solution should contain about 6 g/l. of ferric iron. The iron is eluted with 2 N hydrochloric acid (250 ml., followed by water to a volume of 500 ml.) and determined by titration of an aliquot with standard potassium dichromate solution (after reduction with stannous chloride and so on).

^b The capacities found should not differ by more than 0.3 per cent (cf. Experiment 2, Note ^e).

^c See Experiment 2, Note ^d.

^d If desired, the nitric acid present in the effluent may be determined by any

EXPERIMENTS

- suitable method; hence the capacity of the resin for nitrate ions may be found, and compared with that for chloride and sulphate ions.
- The column should be washed until free from chloride ions and kept for Experiment 5.

Conclusions

A consideration of the results of Experiments 1–4 will indicate a number of factors which have to be taken into account in designing ion-exchange experiments such as, for example, those given in the following chapters. These factors may be summarized as follows:

(1) since the ion-exchange process is a reversible one, which, if allowed to do so, comes to an equilibrium state of incomplete exchange, the complete sorption of a given ion will require excess of resin and will be most readily achieved by a column operation where equilibrium conditions do not prevail;

(2) since the rate of exchange is controlled by film and particle diffusion processes, which are slow, the too rapid passage of a solution through a column will lead to incomplete exchange, or alternatively, will require a proportionately longer column for complete sorption. In general, a compromise is made between rate of flow and efficiency of exchange, but a low efficiency of operation is liable to be uneconomic in industrial practice;

(3) since the regeneration of a resin is essentially the reverse of the loading operation, it is subject to the same laws and hence complete regeneration is only possible with a large excess of regenerant. This point is discussed again in Chapter 7.

Chapter 7

SOME EXPERIMENTS IN SIMPLE COLUMN OPERATION

Introduction

IT WILL be apparent from the concluding remarks of the previous chapter that in the sorption of a metal ion, M^{m+} , by a cation exchanger in the hydrogen form, for example, the metal ions may begin to appear in the effluent from the column before the resin is completely saturated. This arises from the reversible nature of the sorption process which requires excess of M^{m+} ions to complete the reaction



where, as before, the bar over the formula refers to the ion in the resin phase. It is the excess ions which begin to appear in the effluent before the column is saturated (i.e. converted entirely to the M^{m+} form). This effect, which is generally described as a 'break-through' of the ion being sorbed, is the subject of Experiment 5.

When the process is reversed in regeneration, and the metal ions are desorbed under the influence of an acid regenerant, an excess of the displacing ion will likewise be required to effect a complete conversion of the resin to the hydrogen form. The problems involved in the complete regeneration of a cation-exchange column are illustrated by Experiment 6.

The problems involved in the use of anion-exchange columns are so closely related in these respects to those encountered in the operation of cation-exchange columns that separate experiments with anion-exchange columns are not described. However, a suitable scheme for such experiments is indicated briefly for those who may wish to try them.

Experiment 5. The Break-through Capacity of a Cation-exchange Column

A column ($15\text{ cm} \times 1.5\text{ cm}$) containing 5 g of cation-exchange resin in the hydrogen form (50–100 mesh) is required and this should be set up as described in Experiment 4(a) and as illustrated in *Figure 27*. For this experiment it is desirable to have the resin evenly packed so that when a copper sulphate solution is passed down the column at a later stage a sharp horizontal band of copper ions is formed. To achieve this, the rubber connecting tube at the bottom of the column should be closed with a screw clip, the column filled with distilled water, closed with a cork or bung (without any air being trapped) and inverted until all the resin is resting on the cork. On gently righting the column the resin will settle slowly and should form an evenly packed bed. Release the screw clip and allow liquid to drain to a suitable level, as in *Figure 27(b)*, but use a 10 ml. or 25 ml. graduated cylinder as a collecting vessel. An alternative method involves fitting, to the top of the column, a cork carrying a glass tube, which is level with the cork at the bottom but protrudes at the top and is connected by a rubber tube to the waste. The resin bed is then made to rise to just below the cork by an upflow of water of suitable velocity and the flow rate is gradually reduced to ensure even settling of the beads.

Next, draw out the delivery tube of a 250 ml. tap funnel to a constriction like that of a burette nozzle and break it off at that point. By the use of a graduated cylinder and stop watch ascertain how many drops falling from the nozzle in ten seconds correspond to a rate of delivery of 100 ml./h.

Prepare a M/10 solution of copper sulphate (approximately 6.25 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 250 ml. solution) and place 2, 4, 6, 8 and 10 ml. aliquots of this in five dry $\frac{1}{2}$ in. diameter test tubes and in each case make the volume up to 10 ml. by addition of water. These solutions will serve to determine approximately the copper content of the effluent from the column.

Pour the remainder of the copper sulphate solution into the tap funnel and allow it to drop into the column at the rate of 100 ml./h. As soon as 10 ml. of effluent have been

collected in the graduated cylinder, replace it by a second graduated cylinder, and so on, collecting each 10 ml. as a separate fraction. Measure the pH of each fraction with a medium range pH paper (preferably one capable of recording over the pH range 1–5) and estimate its copper content by transferring it to a $\frac{1}{2}$ in. test tube and comparing the depth of colour with the standards already prepared (it is preferable to stand the tubes over white paper and to view the colour through the depth of the tube). As each 10 ml. fraction is collected, record the percentage of the length of the column which has been converted to the copper form—a piece of graph paper, ruled in inches and tenths or in centimetres and millimetres, held behind the column will serve for this purpose. Since the resin at the front of the sorption band will appear green as soon as it is partly converted to the copper form, the value recorded in this way for the percentage of the column length in the copper form will always be too high, but it will serve as a guide.

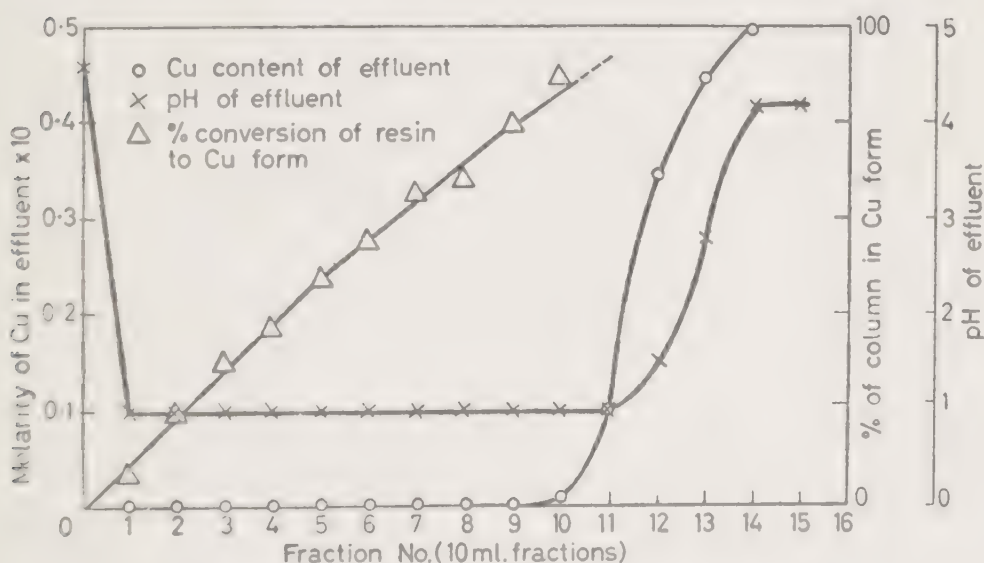


Figure 29. Column break-through experiments

A typical set of results obtained in an experiment of this kind are shown in Figure 29, from which it can be seen that the exchange of copper ions for hydrogen ions leads to a rapid initial fall in pH of the effluent. The pH will not rise again

EXPERIMENTS

to its initial value until all exchange of copper ions for hydrogen ions is complete, when the column is saturated. This will seem to occur in the example quoted at fraction No. 14 (*Figure 29*). This value may be a little high, as the acid generated in the column has to be swept out into the receiver by the passage of a further volume of solution, whilst a lower limit to the fraction corresponding to complete saturation is given as No. 12 by the visual examination of the column. Hence fraction No. 13 may be taken as corresponding closely to the complete saturation of the column, by which stage it will be noted that an appreciable leak of copper into the effluent is occurring. The sigmoidal shape of the copper 'break-through' curve is typical for this type of column operation. At the conclusion of the experiment the column should be washed thoroughly and kept for the next experiment.

An analogous anion-exchange experiment could be based on the sorption of dichromate ions from potassium dichromate solution by the chloride form of a strongly basic anion-exchange resin where the amounts of chloride and dichromate in the effluent could be followed on a semi-quantitative basis. With a resin of light colour the development of the dichromate band could also be followed.

Experiment 6. The Regeneration of a Cation-exchange Column

At the conclusion of Experiment 5, the column used should be entirely in the copper form and so, after it has been washed thoroughly, its reconversion to the hydrogen form may be studied as an example of the regeneration process. This may be carried out with N/2 sulphuric acid solution with a flow rate through the column of 100 ml./h and the copper content and pH of each 10 ml. fraction of the effluent should be measured as in the preceding experiment. Since the regenerating solution is stronger than M/10, the copper content of the effluent may also rise above this value at some stage so that a series of standard copper sulphate solutions prepared by dilution of, say, an M/2 copper sulphate solution in addition to those already prepared, will be required for purposes of comparison.

Results obtained in a typical experiment are shown as full curves in *Figure 30*, from which it is evident that a break-through of acid accompanies the removal of the bulk of copper and that the last traces of copper are removed from the column only after the passage of a large excess of acid through it. The effect of the use of different strengths of acid

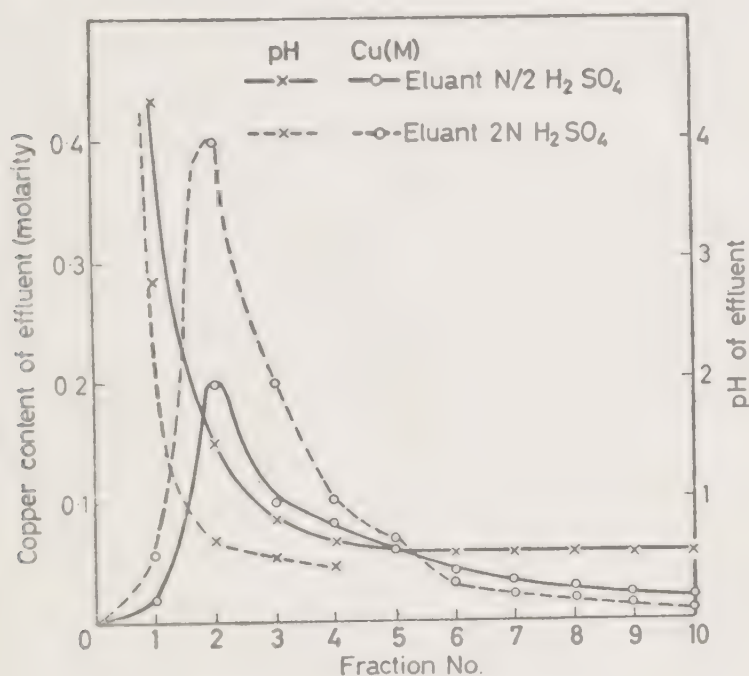


Figure 30. Elution experiments

solution for the regeneration process may be established by washing the column, reloading it with copper ions, as in Experiment 5, washing it again and then repeating the experiment but with a stronger sulphuric acid solution. The results obtained with 2 N sulphuric acid are shown by the broken curves in *Figure 30* and from these it is apparent that whilst the use of a stronger solution of the acid removes the bulk of the copper a little more rapidly, the 'tailing' of the last traces of metal ions from the copper is hardly reduced at all. Furthermore, a high proportion of the acid accompanies the copper in the effluent and is thus wasted.

The regeneration of an anion exchanger in the dichromate form (see Experiment 5) with N/2 sodium hydroxide solution

EXPERIMENTS

—yielding in fact the free base and not the original chloride form—could be followed on a semi-quantitative basis. It would be necessary to neutralize the alkali present in the effluent fractions with acid and to adjust the pH further to coincide with that of the dichromate solutions used as colorimetric standards. This regeneration process is an interesting one since the removal of the dichromate is accompanied by a change to chromate.

Conclusions

In Experiment 5 the bivalent copper ions are more firmly held by the resin than the univalent hydrogen ions and hence the break-through of copper ions is delayed until the column is almost saturated. If the ion being sorbed had been univalent, e.g. sodium, then an earlier break-through would have been expected. The relative affinities of sodium and hydrogen ions for the resin are closer than those of copper and hydrogen ions and hence the driving force in the left to right reactions is less in the case



than in



and accordingly the tendency for the sodium ions to be held will not be so great, particularly after the resin is partly saturated.

The efficiency of a column is therefore markedly dependent on the nature of both the ions sorbed on the resin initially and those sorbed during the exchange process. In fact, it can be seen from the results obtained in Experiment 6 that the sorption of hydrogen ions on a column initially in the copper form is a very inefficient process characterized by an early break-through.

The relative affinities of several ions under standard conditions have been determined, although some are known only qualitatively, but in no case are relative affinities known for the whole possible range of solutions, concentrations and degrees of saturation of the resin. Furthermore, the presence in the solution of complexing agents which will react with one of the exchanging ions to form complex ions, will lead to

apparently anomalous values for relative affinities of the ions. Hence before designing a column for a given process it is highly desirable to carry out first an experiment on the lines of Experiment 5, but conforming as closely as possible to the conditions (of concentrations of solutes, temperature, etc.) under which the process is to be carried out.

Since the operating, or loading, stage of ion-exchange column operation is most effective when the ion being sorbed is more firmly held than the ion being displaced, as is the case in Experiment 5, it naturally follows that in many cases, columns will be used under these conditions; hence the process of regeneration will be more difficult and less efficient as is the case in Experiment 6. From the reversible nature of the exchange process, the desorption of copper, for example, will tend to occur more readily as the concentration of the displacing hydrogen ions increases (cf. *Figure 30*), but despite this, the removal of the last traces of the sorbed metal ions is always slow, and is hardly achieved any more readily by the use of stronger acid.

In laboratory applications where the cost of regenerant materials is unlikely to be an important factor, it may be convenient to use a stronger regenerant solution, but in large scale operation the correct choice of regenerant strength will be important and preliminary trials on the lines of Experiment 6 will be essential. The use of a 'gradient regeneration' with a regenerant of high initial concentration of acid which is continuously diminished during the process might well be considered in such a case.

The use of an unnecessarily strong regenerant solution should always be avoided. A resinous exchanger which will be fully swollen in water will shrink again as the concentration of electrolyte present is raised from zero to high values. As a result of the shrinkage of the bead, the diameter of the pores in it will decrease and the migration of ions within the bead impeded to some extent. In very concentrated electrolytes, therefore, the rate of exchange may be adversely affected and in the case of larger ions, such as the hexamminocobalt (III) ion completely impeded. Where the use of a strong regenerant solution cannot be avoided it may be advantageous to use a

EXPERIMENTS

resin with a lower degree of cross-linking than normal, but it must be remembered that there will be a bigger change than usual in the swollen size from the operating or regenerating stages to the washing ones, or vice versa.

The regeneration experiment suggested as an example of anion-exchange operation is of interest in that in it there is a chemical change accompanying the desorption of the dichromate, namely its conversion to chromate in the alkaline medium



and



Changes of this type are always liable to occur when a change in the medium occurs, in pH for example, and such effects must always be taken into account. They may be helpful, as in the case of the dichromate-chromate change, where the desorption of the chromate ion is probably more easily achieved than the desorption of dichromate; on the other hand, they may not, as in the case of precipitates formed in or on the resin.

In the experiments described in this chapter, studies of the effects of changes in flow rate, temperature, and electrolyte concentration have not been included, but the importance of such studies in ascertaining optimum column operation conditions will be evident.

Chapter 8

SIMPLE ION-EXCHANGE PROCEDURES COMMONLY EMPLOYED IN ANALYSIS

Introduction

IN THE analytical uses of ion exchange it is generally a requirement that one or more ions are completely retained by the exchanger. Thus an ion which is not easily determined, such as the sodium ion, may be exchanged for one which is, such as hydrogen, but the exchange must be complete if it is to be used as the basis for an analytical method. Alternatively, if it is necessary to determine the amount of borate in a sample containing an interfering ion such as iron (III) or aluminium, the interfering ion must be effectively removed first; this too may be achieved by ion exchange.

It is essential, therefore, that an excess of resin be used. In other words, the full capacity of the column is never employed, and furthermore, the resin must always be fully in the hydrogen (or other selected) form and must be fully regenerated and washed after use and before re-use. Otherwise in the determination of sodium ions by their replacement with an equivalent of hydrogen ions, for example, the hydrogen ions liberated by the exchange process at the top of the column may subsequently exchange at the bottom of the column with sodium ions left from a previous operation. In such a case the hydrogen ion content of the effluent will be less than equivalent to the sodium ion content of the original solution, and similarly any reagent left from incomplete washing of the resin will cause inaccuracies.

The concentration of the solution to be treated should not be too high, particularly when a cation exchanger is used in the hydrogen form or an anion exchanger in the hydroxide

EXPERIMENTS

form. In the first case, the acid liberated in the exchange process may lower the pH of the solution to a value (*ca.* pH 1–2 for exchange with univalent ions, or lower with polyvalent ions) where the exchanger tends to revert to the acid form, while in the second case the pH rises to a value (*ca.* pH 11–12) where the exchanger reverts to the hydroxide form. As a result the exchange processes will become inefficient.

The rate of flow of the test solution through the column must obviously be slow enough for complete exchange to occur, but if ion exchange procedures are to compete effectively with alternative analytical methods a rate of flow of at least 100 ml./h through a bed of 50–100 mesh beads 10 cm long by 1.5 cm diameter should be achieved. Any lowering of column efficiency resulting from a high rate of flow can be offset, to some extent, by the use of a longer column, but there is a limit to what can usefully be achieved in this way. After the test solution has been passed through the column it must be followed by a volume of water sufficient to displace all the electrolyte from the column. With the type of column arrangement advocated in *Figure 27*, where the column forms, in effect, one arm of a U-tube, the volume of water required is proportionately larger than with columns of the straight-through type, but this disadvantage is compensated by the advantage that the column cannot run dry if it is left.

The two main types of analytical applications of ion exchange other than chromatographic ones are illustrated in Experiments 7 and 8. As in the previous chapter the experiments selected are based on the use of cation-exchange columns. However, a scheme for an experiment with an anion-exchange column is outlined under Experiment 7, and in addition a modified procedure for the treatment of an 'insoluble' substance using a cation exchanger.

Experiment 7. Determination of Total Salt Concentration

A column (15 cm × 1.5 cm) containing 5 g of cation exchanger (strongly acidic type, normal cross-linking, 50–100 mesh) as used in Experiments 5 and 6, is again required, and the tap

funnel with the drawn-off tip; in addition a 500 ml. conical flask is required as a receiving vessel.

A suitable test solution is one containing sodium sulphate (approximately M/40, circa 3.5 g/l. Na_2SO_4) and copper sulphate (approximately M/40, circa 6.25 g/l. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). Both should be weighed out and the solution containing them made up to a given volume so that the concentrations of each are accurately known (analytical grade reagents should be used).

Transfer a 25 ml. aliquot of the mixed solution to the tap funnel (see Experiments 5 and 6), dilute to about 100 ml. with water and allow it to drip through the column at a rate of 150 ml./h, collecting the effluent in the 500 ml. conical flask. Follow this with four successive 50 ml. (approximately) portions of water—without changing the receiver—taking care each time to wash down the sides of the tap funnel with water and allowing each portion of wash water to drain completely from the tap funnel before adding the next. After the first portion of wash water has passed through the column, rinse round the wall of the column above the resin bed and allow the column to drain to its normal level before adding the second portion of water to the funnel.

Titrate the acid present in the combined effluent and washings with standard (approximately N/10) sodium hydroxide solution with phenolphthalein as indicator. Calculate the concentration of sulphate, as g/l. $\text{SO}_4^{=}$, present in the solution. If the copper concentration is determined on a separate aliquot of the test solution, it is then possible to deduce the concentrations of copper sulphate and sodium sulphate present. These values may be compared with those derived from the quantities weighed out and the volume of the test solution.

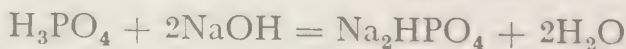
The column should be completely regenerated with excess of 3 N acid and then washed thoroughly—until washings are neutral to methyl orange indicator—before further use; a backwash to loosen the resin bed should be included at one stage.

An analogous anion-exchange experiment could be based on the treatment of a 25 ml. aliquot of a solution containing

EXPERIMENTS

potassium nitrate (approximately M/20) and potassium carbonate (approximately M/40)—both present in known concentrations—which should be passed through a column (15 cm × 1.5 cm) containing 5–6 g of strongly basic anion-exchange resin in the hydroxide form. For this purpose the regenerated column (OH form) from the anion-exchange experiment outlined at the end of Experiment 6 would be suitable if it were washed with boiled-out distilled water until free of regenerants (washings giving no colour with phenolphthalein indicator). The combined effluent from the test solution and subsequent washings should be titrated with standard hydrochloric acid solution (approximately N/10) with methyl orange as indicator. A similar titration with a separate aliquot will give the carbonate content of the test solution and hence the potassium nitrate content of the solution may be derived.

An extension of the cation-exchange experiment which is occasionally useful is one where an 'insoluble' substance is analyzed. Weigh accurately into a 250 ml. conical flask about 0.5 g of commercial cobalt phosphate and add to it 150 ml. water and approximately 3 g strongly acidic cation exchanger (hydrogen form, 50–100 mesh). Stopper the flask firmly with a rubber bung and place it on a mechanical shaker until no phosphate remains in suspension. Stop the shaker, wash the bung and neck of the flask with a jet of water so that the washings drain into the flask, and decant the contents of the flask carefully (preferably through a 3 in. funnel) into a column (15 × 1.5 cm) containing approximately 3 g of the same cation-exchange material (see *Figure 27* for arrangement of column), collecting the effluent in a 500 ml. conical flask. Wash the smaller flask, and any resin remaining in it, with five successive 15 ml. portions of water and decant each slowly into the column. Titrate the combined filtrate and washings with standard (approximately N/10) sodium hydroxide solution with phenolphthalein indicator, when the end point will correspond to the stage of neutralization.



Calculate the percentage PO_4 in the sample of cobalt

phosphate and, if possible, compare the result with that obtained by a gravimetric determination of the phosphate.

Transfer any resin adhering to the walls of the small flask to the column by means of a jet of water. Pass 100 ml. of 2 N nitric acid from a tap funnel through the column at a rate of 50 ml./h, following this with 50 ml. water (at 100 ml./h) and collecting the effluent in, say, a 250 ml. beaker. Determine the cobalt content by any convenient method and calculate the composition of the phosphate.

Experiment 8. The Removal of an Interfering Ion

This experiment requires the same type of cation exchange column, and other apparatus as those used in Experiment 7. The test solution should be prepared by weighing out accurately into a 250 ml. beaker, about 3.5 g borax and adding 60 ml. water. The contents of the beaker are stirred until as much as possible of the borax is dissolved, a few drops of methyl orange indicator are added and then a solution of hydrochloric acid (*ca.* 1 N) is added slowly from a burette, whilst the suspension is stirred, until the solution is just acid in reaction to the indicator. Finally, add approximately 2.5 g copper sulphate pentahydrate and stir until this has dissolved before transferring the solution to a 250 ml. graduated flask and diluting it to volume.

Transfer a 25 ml. aliquot of this solution to the tap funnel and allow this to drip through the column at a rate of 150 ml./h. Wash the funnel with four successive portions of water, each about 25 ml., and rinse round the top of the column following the procedure described in Experiment 7. Collect the washings with the main effluent in a 500 ml. conical flask. Add two to three drops of methyl orange and titrate the solution with standard (approximately N/10) sodium hydroxide solution. Add 2–3 g mannitol and a few drops of phenolphthalein and titrate again with the standard sodium hydroxide solution to an end point which is unaffected by further additions of mannitol. From the second titration calculate the concentration of borax in the test solution and compare the result with that calculated from the quantity of borax weighed out. An error of some 2 or 3 per cent may

EXPERIMENTS

occur using this simple procedure; a more detailed procedure capable of dealing with a wide range of interfering ions is described by Martin and Hayes¹.

Conclusions

The procedure employed in Experiment 7 in which the cations are replaced by hydrogen ions (or the anions by hydroxyl ions) in equivalent amount provides a useful method for the determination of the total salt concentration of a neutral solution. It is applicable to solutions containing one electrolyte (e.g. sodium sulphate alone) or more than one, as in the experiment described here. This method of substitution is particularly useful in the analysis of soluble perchlorates, acetates and similar salts where there is no simple procedure for the determination of the anion as well as for the determination of alkali metal salts. However, in the authors' experience it is not possible to get such reliable results with the anion-exchange procedure as with the use of a cation exchanger. Hence experiments should be designed to use cation-exchange columns where possible.

In the case of replacement of the cations by hydrogen ions any free acid present in the test solution will pass into the effluent and will be titrated together with the acid liberated by the exchange process. Similar considerations will apply in the replacement of the anions by hydroxide ions. It is sometimes possible to make a correction for the free acid or base initially present, if this can be determined, while in other cases it is possible to carry out a differential titration on the effluent, for example when a borate is to be determined in the presence of a strong acid.

It may also be noted that the test solution proposed for an anion-exchange experiment analogous to Experiment 7 would not be suitable for treatment by a cation-exchange procedure; exchange of the potassium ions for hydrogen ions would lead to formation of the unstable carbonic acid. Similarly, solutions containing nitrites can be treated by the anion-exchange method only, whilst certain heavy metal salts which would yield insoluble hydroxides with the anion-exchange procedure, can only be treated by the cation-exchange method.

There are evidently a number of restrictions on the use of the procedure of Experiment 7 and the following are among the more important conditions which must be fulfilled for its successful application:

(1) The test solution must: (a) contain only substances which are in true solution—any colloidal matter such as metallic hydroxides might precipitate on the resin or pass into the effluent, either of which would be objectionable. Many heavy metal salts which hydrolyze in water cannot be treated easily (the difficulties attendant upon the addition of free acid to suppress hydrolysis have already been indicated); and (b) contain no complexes in which anions are bound to the metal ions by forces strong enough to hinder the free and complete exchange of either in simple form—i.e. not as complex cations or anions. For example, in the treatment of certain phosphates containing some iron (III), a part of the phosphate may under certain conditions be retained on the cation exchanger as the complex FeHPO_4^+ ion.

(2) The product or products of the exchange process must be: (a) soluble and stable in water—the production of an insoluble acid or base must be avoided; and (b) unreactive towards the resin—modern ion-exchange resins are remarkably inert, but are liable to be affected by strong oxidizing agents such as permanganic acid. Most cation-exchange resins seem to possess some reducing properties, but in the case of those based on polystyrene this can be reduced to negligible proportions by one or two treatments with dilute (10 per cent w/w) chromic acid (not chromic-sulphuric acid cleaning mixture) with intermediate stripping of chromium (III) from the resin with acid.

Usually these difficulties can be avoided in many instances by suitable choice of conditions, for example, by the use of an anion-exchange column in place of a cation-exchange one in the case of solutions of carbonates or nitrites. It is possible in some cases even to overcome the difficulties encountered with readily hydrolyzable substances by treating them by a modified form of the procedure described for the treatment of 'insoluble' materials. The resin is added to the dry salt before the water, which is then added very slowly with constant

EXPERIMENTS

shaking; in this way the acid liberated in the first stages of the exchange serves to suppress the hydrolysis of the compound. Stubborn cases, such as stannous chloride, will not respond to this treatment, however.

The treatment of an 'insoluble' compound described in Experiment 7 is based on the fact that no compound is absolutely insoluble. If the solubility product is not too low an 'insoluble' substance will, in contact with water, yield sufficient ions for exchange with the resin to take place. Thus cobalt phosphate will yield a few cobalt (II) and phosphate ions of which the former will exchange with hydrogen ions from the exchanger to yield phosphoric acid. In this case the acid liberated has some solvent action on the insoluble phosphate, thus helping the process, but in many instances the solubility of the insoluble substance is depressed still further by the common ion effect and the volume of water used must then be kept large enough to keep the acid concentration to a minimum. It may be noted that barium sulphate can be treated by this procedure if it is freshly precipitated, but it is much more difficult to bring an aged precipitate or dried material back into solution.

In Experiment 8, the presence of the coloured cupric ion would cause interference in the direct volumetric determination of the borate and the ion-exchange procedure provides a very convenient method for its removal. The procedure described in this experiment is capable of very wide application, particularly when advantage is taken of changes which may occur in the state of charge of a metal with changes in either its oxidation state or its co-ordination condition. Thus chromium (III) present as a cation is not readily separated from other cations, but on oxidation to chromium (VI) it will yield chromate or dichromate ions, which may be sorbed on an anion exchanger or left in solution whilst other cations which are not affected by the oxidation [e.g. aluminium or iron (III)] are sorbed on a cation exchanger. Similarly, iron (III) is converted by excess of thiocyanate ions to a complex $[\text{Fe}(\text{CNS})_6]^{3-}$, which is sorbed by an anion exchanger whilst aluminium is unaffected by the presence of the thiocyanate and remains as a cation. Hence a separation can be effected

and the aluminium can be determined after the removal of the ion².

The conditions required for the successful application of the procedure of Experiment 8 are very similar to those for Experiment 7 and include:

(1) The test solution: (a) must contain only substances which are present in true solution—in this case (cf. Experiment 7) it is permissible to suppress formation of colloidal hydroxides by the addition of acids provided that the pH is not lowered too much thereby; and (b) must not contain complexes which will interfere with the separation being attempted—as distinct from those which are deliberately formed to make the separation possible as in the iron-aluminium separation just mentioned.

(2) The product or products of exchange must again be: (a) soluble and stable in water; and (b) unreactive towards the resin.

Numerous examples of the analytical uses of the methods of Experiments 7 and 8 have been quoted in the literature³ and need not be repeated here, since the present object is to provide some detailed account of the basic procedures which are not generally quoted. If experiments are designed on the basis of the models given in this chapter and the conditions are correctly chosen, few difficulties should be encountered, but where trouble is encountered it is wise to apply the following checks:

- (1) The column is large enough (contains sufficient resin) to ensure 100 per cent exchange and that it is uniformly packed and free from air bubbles.
- (2) The rate of flow through the column is not too high.
- (3) An adequate volume of wash water is used to displace the products of the exchange completely from the column to the receiver.
- (4) The column is given adequate regeneration and washing (preferably with a backwash at one stage) after use and before re-use.

EXPERIMENTS

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Chapter 9

APPLICATIONS OF ION EXCHANGE IN PREPARATIVE CHEMISTRY AND IN PURIFICATION AND RECOVERY PROCESSES

Introduction

THE applications of ion exchange described in this chapter involve procedures which closely resemble those described in the two preceding chapters. Thus in the field of preparative chemistry, ion exchange may be used in the preparation of free acids or bases from suitable salts or in the preparation of one salt from another by the process of exchange of one cation for another (e.g. hydrogen ion in the preparation of an acid) or of one anion for another (which would be hydroxide in the preparation of a base) by a procedure of the type in Experiment 7.

In the purification process, the objective—the elimination of unwanted ions—is the same as that of Experiment 8 and the procedure followed is essentially the same. One important difference, however, is that for economic reasons it is not desirable to use a small fraction of the column capacity only, as in Experiment 8; the column is operated to the point of break-through before regeneration which must be achieved with the minimum possible quantity of regenerant. Hence, experiments of the pattern of those of Experiments 5 and 6 must be performed to establish optimum operating conditions.

The experimental conditions required for the two experiments given in this chapter and the precautions to be observed in carrying them out are consequently the same as those given for Experiments 5–8 inclusive and will not be repeated in detail. To avoid confusion, the same type of column (15 cm long \times 1.5 cm diameter) with 5 g air-dried exchanger (50–

EXPERIMENTS

100 mesh, normal cross-linking) will again be used for the basic experiments; a suggested scaling up of the demineralization of tap water is indicated in Experiment 10.

No separate example of a recovery process is given since it differs from the purification process only in that the ion sorbed on the resin is wanted, instead of an unwanted impurity. The regeneration of the resin when it is loaded must therefore be carried out in such a way as to obtain the recovered material in the most convenient form possible.

Experiment 9. Uses of Ion Exchange in Preparative Chemistry

(a) *Preparation of an acid*

Repeat Experiment 7, but in place of the test solution used there use a 25 ml. aliquot of one containing approximately 20–25 g/l. of analytical potassium ferrocyanide [$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$]. It is essential that a high grade distilled water free from carbon dioxide be used in the preparation of this solution. The strength of the test solution should be known either from the weight of ferrocyanide used in its preparation, or preferably from standardization of an aliquot against a ceric sulphate solution standardized previously against sodium oxalate.

The combined effluent and washings from the cation-exchange column may be titrated with 0.25 N sodium hydroxide solution, either potentiometrically using a glass electrode–saturated calomel electrode system with a valve voltmeter or directly using methyl orange as indicator. If the latter method is used the column should be regenerated with, say, 500 ml. 2 N acid and washed thoroughly, a further aliquot of potassium ferrocyanide solution treated, and the effluent and washings titrated with the same sodium hydroxide solution, but with an indicator responding to a different pH range. In this way an estimate of the strengths of the various stages of ionization of ferrocyanic acid may be obtained.

(b) *Preparation of a base*

The properties of hexamminocobalt (III) hydroxide prepared by the use of an anion exchanger in the hydroxide form from

a solution of hexamminocobalt (III) chloride may likewise be studied¹.

(c) *Preparation of salts*

Both cation- and anion-exchange processes can be used, at least in theory, for the conversion of one salt of a metal to another. Thus a solution of ferric perchlorate, which does not appear to be readily obtainable commercially, may be obtained in a state of high purity (but containing some free perchloric acid) from analytical grade ferric chloride. A column of strongly acidic cation exchanger (5 g) is saturated with iron (III) ions by the passage through it at about 150 ml./h of excess of a solution of ferric chloride (circa 0.1 M, the solution must be clear and the pH should be adjusted to circa 1 if higher than that, by addition of HCl). The column is washed until the washings are free from chloride and then 10 ml. 1 N perchloric acid, followed by 40 ml. water, are passed through it at a rate of 50 ml./h. Under these conditions there will be an excess of iron, which will remain on the column, and hence as the acid is displaced down the column by the wash water it is continually coming into contact with fresh resin in the iron (III) form. Hence the reaction:



is driven to the right and the resulting solution should not contain a great excess of free acid [iron (III) salts will of course always give an acid reaction in water]. If excess of acid is used the ion sorbed on the column will be completely recovered, but the proportion of free acid in the resulting solution will be higher.

In this case the apparently more convenient method of passing ferric chloride solution through a column of anion-exchange resin in the perchlorate form is not, in fact, as convenient since the relative affinities of chloride and perchlorate ions are such as to favour retention of the latter on the resin. Accordingly the conversion to perchlorate may be incomplete and the product contaminated with chloride unless the size of the column of perchlorate form resin is very

large in comparison with the bulk of solution to be treated, which would cause difficulties in manipulation.

Experiment 10. The Demineralization of Water: An Example of Ion-exchange Purification

This experiment is, in its initial stages at least, based on Experiment 5 and involves the same procedure. The main difference is that the test solution is hard tap water (preferably 200–300 p.p.m. total hardness as calcium carbonate). The break-through of calcium (plus magnesium) ions may be followed by collecting 50 ml. fractions of the effluent and determining the total hardness present in them by the method quoted by Martell and Calvin². Plot the results obtained as in Experiment 5 and on the basis of the assumption that water containing not more than 10 p.p.m. of total hardness at any stage would be acceptable, deduce the volume of the tap water being used which can be treated by this column.

Wash the column briefly with an upward flow of tap water to loosen the resin particles and to displace foreign solid matter from the column (see Experiment 1 and *Figure 24* for details) and regenerate the column using 2 N hydrochloric acid. In order to arrive at a suitable regenerant volume, it may be assumed that the relative affinities for the pairs of ions $\text{Cu}^{++}-\text{H}^{+}$ and $\text{Ca}^{++}-\text{H}^{+}$ (with 2 N acid as the aqueous phase) will not differ greatly (cf. *Figure 30* broken curves) and that the volume can be based on the results of Experiment 5. Wash the column with distilled water until free of acid and test that the volume of acid used for regeneration was adequate by repeating the loading cycle. If the volume of tap water which can be treated before hardness of the effluent rises to the limit of 10 p.p.m. is less than before, then the volume of reagent used must be increased, otherwise it is adequate and may possibly be reduced. By process of trial and error find the minimum quantity of acid which can be used to give full efficiency in the loading cycle.

Once the operating conditions for the cation-exchange column have been established, those for an anion-exchange column, to remove the acids liberated by the cation exchanger,

must also be ascertained. A column (15×1.5 cm) containing 5 g of anion exchanger (air-dried, chloride form, strongly basic, 50–100 mesh) should be used. The resin should be converted to the carbonate form, by the passage through the column of 1 M sodium carbonate solution, until the effluent is free from chloride; the volume of carbonate solution required to achieve this should be noted and will provide a rough guide as to the amount of sodium carbonate solution to be used in the subsequent regeneration of the column. Wash the column with distilled water until the washings give no colour with phenolphthalein indicator.

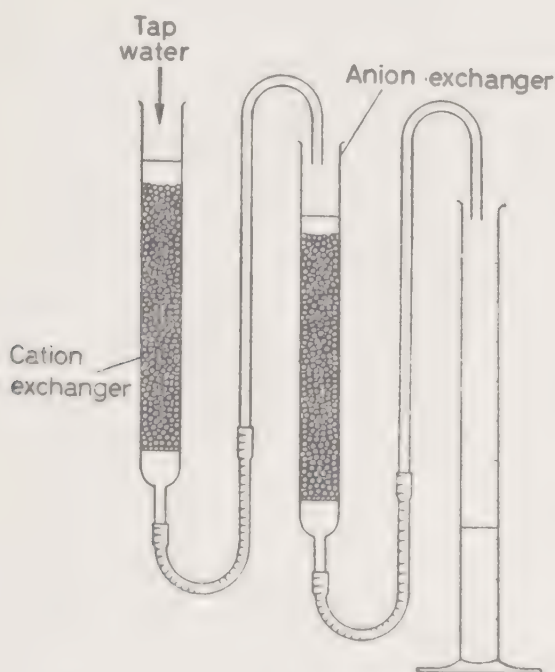


Figure 31. Two-stage de-ionization

With the cation exchanger in the fully regenerated and washed form and the anion exchanger in the washed carbonate form, pass the tap water to be treated first through the cation-exchange column and thence into the anion-exchange one (see Figure 31 for arrangement of columns) and collect the effluent until that emerging from the anion-exchange column

EXPERIMENTS

shows an acid reaction to bromothymol blue or the maximum volume of water that can be treated by the cation exchanger has passed through it. If the latter occurs stop the process and regenerate and wash the cation-exchange column before proceeding with the experiment to the point of break-through of acid from the anion-exchange column. By addition of a known weight of resin (hydrogen if to the cation-exchange column, chloride form if to the anion-exchange one) to one of the columns, make the quantity of water which each column can treat in one operation more nearly equal.

Wash each column separately by a short upward flow of water as described above and regenerate and wash them thoroughly. As already indicated, the quantity of 1 M sodium carbonate used to convert the column to the carbonate form originally will provide some indication of the volume of regenerant required for that column. Any change in weight of resin in the columns must be allowed for in the regeneration process. As with the regeneration of the cation exchanger, the minimum quantity of regenerant required for the anion-exchange column can be established by trial and error.

Once the other operating conditions have been established, the rate of flow through the columns may be increased from 100 ml./h to, say, 150 or 200 ml./h and so on until a stage is reached where an earlier break-through of either metal ions from the cation exchanger or of acid from the anion-exchange column is detected. An optimum flow rate may thus be established.

Next, design a larger scale demineralizing plant using the larger columns (60 cm long, 4.5 cm diameter) used in Experiment 1 with not more than 500 g of resin in either column—with the amounts of resins used kept in the optimum ratio already established. Approximate indications as to the quantities of regenerants can be obtained by a direct scaling up of the quantities used before, and as to the maximum flow rate by comparing the areas of the resin beds in the large and small columns and using this ratio as a scaling factor. However, as the scaling up is not an exact one with regard to column dimensions, further checks as to the optimum operating conditions will be needed.

The demineralized water obtained from this two column plant will be suitable for many analytical purposes and will not contain much carbon dioxide since up to the point where the effluent of the second column gives an acid reaction to bromothymol blue the acid generated in the cation-exchange column converts the carbonate sorbed on the anion exchanger into bicarbonate, e.g.



Any remaining impurities present in this water can be reduced to an even lower level by passing the demineralized water obtained from the first two columns through a second cation-exchange column in the hydrogen form and then through a second anion-exchange column, which should be in the hydroxide form. A more effective method involves the use of a single column only to remove these remaining impurities. In this case the column contains a mixture, obtainable commercially, of cation-exchange resin in the hydrogen form and anion exchanger in the hydroxide form. This column will reduce the concentration of cationic and anionic impurities, including carbonate and silicate, to a very low level. Care is required in filling the column with the mixed resin since, as the two resins differ in density, they settle at different rates in water and the effectiveness of this 'mixed bed' column depends on the two resins being kept in an intimate mixture. The column should be filled by a reverse (i.e. an upward) flow of water, to displace air from below the disc, to about two inches above the disc and sufficient resin tipped into the column to bring the top of the resin level with the surface of the water; the water level should then be raised another two inches, by either upward flow or by addition from above—but in either case without disturbing the resin already added—more resin added, and so on. When the column has been filled, the hydroxide form anion-exchange resin must be protected from the carbon dioxide of the air and the column should be fitted with a bung and delivery tube with a suitable connection to the outlet from

EXPERIMENTS

the anion-exchange column or to the reservoir in which the water obtained from the first two columns is stored (see *Figure 32* for a suggested arrangement).

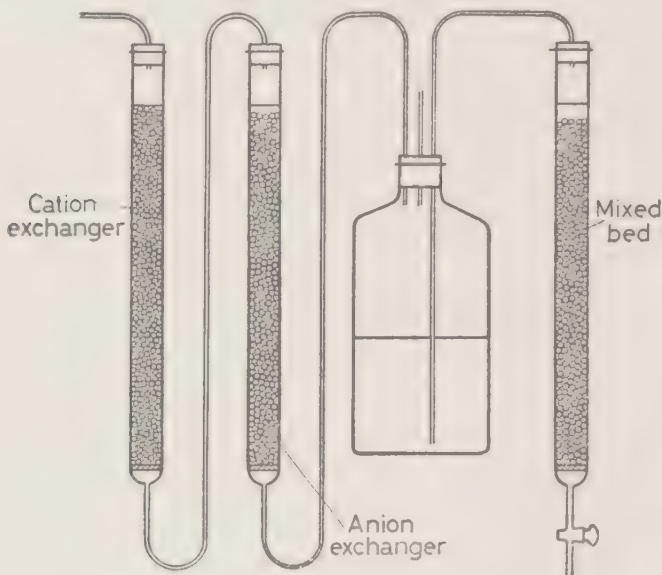


Figure 32. Two-stage de-ionization with final mixed bed column

The quality of the water from the three column system should be as good as that of 'equilibrium' water or, initially, even better and its quality is in fact best checked by a determination of its specific conductivity. Provided the first two columns are always regenerated as soon as they are exhausted, the life of the resin in the third column will be high. Consequently it does not generally add unduly to the operating costs if the mixed bed resin is thrown away when exhausted, and replaced—the regeneration of a mixed bed column is not readily achieved with small laboratory columns.

Conclusions

The experiments quoted in this chapter represent a few of the many types of applications of ion exchange in the processes of preparation and purification. The preparation of an acid from one of its salts by ion exchange is a particularly useful

one which is much more convenient than the use of the classical methods, and we have had occasion to use it more than once. Likewise we have found the method given for the preparation of ferric perchlorate a very convenient one.

The details of experimental procedure in other applications in this field will be dependent on other conditions inherent in the experiment (e.g. solubility of starting materials or products) so that Experiments 9 and 10 can be regarded as general models only for other processes of preparation, purification, or recovery. Whether the ion-exchange method is the best one for a given process must be a matter for experience; we believe that the examples given in this chapter represent cases where the ion-exchange procedure is the most convenient one.

The demineralization of water is one of the most widely used applications of ion exchange and was the obvious choice for the example of a purification process and one which was strengthened by the many requests the authors have received for the ion-exchange method for obtaining distilled water. However, since all the experiments have, for the sake of simplicity, been based on strong acid and strong base resins, we have suggested the use of a strong base resin in Experiment 10 in place of the weak base resins commonly employed for this purpose. One advantage is that the property of imparting a colour to the solution, which is shown by some weak base resins, is avoided by the use of the strongly basic exchanger.

Because of the difficulties which may be encountered in the regeneration of the anion-exchange resin with sodium hydroxide, the use of the resin in the carbonate form is advocated. As mentioned, the acid generated in the cation-exchange column will at first convert this to bicarbonate which will remain sorbed by the exchanger, and beyond this point any carbonic acid from the first column will not be sorbed, whilst any sulphuric or hydrochloric acid will, in fact, displace bicarbonate from the exchanger. Hence from this point, when the effluent becomes acid to bromothymol blue to the point where strong acid (H_2SO_4) breaks through, a further quantity of water can be obtained which will contain only carbon dioxide as a major impurity. This may be used

EXPERIMENTS

as such if it is suitable, but should not be passed through a mixed bed column unless most of the carbon dioxide is removed first by bubbling a rapid stream of air through it, otherwise the life of the mixed bed column will be greatly reduced. Those who are interested primarily in producing demineralized water, rather than in following Experiment 10, will find that resin manufacturers are generally willing to provide details of column set-up and operation.

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Chapter 10

ION-EXCHANGE CHROMATOGRAPHY

Introduction

THE separation of the lanthanons (rare earth elements) by ion-exchange chromatography is probably the best known application of ion exchange. However, the technique of ion-exchange chromatography is not an easy one, particularly for those unfamiliar with the properties of ion-exchange materials and for that reason the subject has been deferred to the penultimate chapter.

Although it is in many ways similar to other forms of chromatography, ion-exchange chromatography differs in that the sorption and ion exchange take place right through the resin beads and also in that the beads may shrink or swell with changes in the nature of the liquid phase.

Since it is essential in chromatographic applications that at any point in the column at any instant, equilibrium conditions (or a very close approach to them) shall prevail, it is imperative that the flow rates in the elution or displacement stages are kept as low as possible. To lessen the time for the exchanging ions to diffuse in and out of the beads, and hence for equilibrium to be established, it is advisable to use beads of small diameter. This reduces the effects of particle diffusion and also, by increasing the ratio of surface area to volume of resin, those of film diffusion. However, if very fine beads are used these tend to pack very tightly and thus impede the flow of liquid through the column. For this reason it is suggested that the beginner uses, in the first instance, beads of 50-100 mesh and defers the use of finer beads (100-200 mesh or even smaller) until some preliminary experience has been gained.

It is of particular importance in chromatography to have a resin bed of uniform packing, since any tendency for liquid to 'channel' when flowing through the column will lead to the

EXPERIMENTS

formation of irregular bands and hence to poor separations. Sudden large changes in the strength of the electrolyte in the column should therefore be avoided during the separation process, otherwise shrinkage or swelling of the resin may occur unevenly in the bed, and so upset the packing. For this reason resins of low degree of cross-linking (i.e. less than 4 per cent D.V.B.) which are particularly susceptible to such changes should not generally be used. On the other hand, if very tightly cross-linked resins are used, particle diffusion may become a rate-controlling stage in the exchange process, particularly when exchange of large ions is involved. Care must be taken to ensure that at no time in the loading or elution stages is the column subjected to uneven heating effects from sunlight, radiators or bunsen burners.

The two procedures of displacement and elution chromatography do not differ greatly from the point of view of technique, and since the latter is the more widely used, the experiment given in this chapter is based on the elution method.

Experiment 12. Preliminary Studies in Ion-exchange Chromatography

A column (15×1.5 cm) containing 5 g of cation exchanger (strongly acidic, normal degree of cross-linking, 50–100 mesh) may again be used. After complete conversion of the resin to the hydrogen form has been effected (if necessary) and thorough washing of the column completed, an even packing of the resin bed must be achieved. Two methods by which this may be done have already been described in Experiment 5 and need not be repeated.

Place a small Gooch crucible disc, of diameter slightly smaller than the column on top of the resin bed. This will prevent disturbance of the resin beads by liquid dripping into the column. The procedure for loading the column is similar to that given in Experiment 5, except that only 25 ml. of M/10 copper sulphate solution is used. This is followed by 100 ml. water to displace the sulphuric acid liberated in the exchange process. At this stage a sharply defined blue-green band of copper ions with a sharp, horizontal, lower edge

should be clearly visible. If this is not the case, it will be necessary to regenerate the column, wash and resettle the resin bed before reloading.

Once the sharp copper band has been established at the top of the column and the column has been washed, pass a solution of hydrochloric acid of pH 0.5 through the column. If a pH meter is not available prepare a solution as close to pH 0.5 as can be judged with a narrow range pH paper, and to avoid variations of pH in a series of experiments prepare at least 2 l. and use this as a stock solution. The rate of flow should be 50–60 ml./h and the effluent collected—each 10 ml. fraction separately—in graduated cylinders or by fraction cutter. If the column has been well packed, the lower edge of the band will remain sharp and horizontal as it moves down the column—the experiment will otherwise have to be restarted!

Record the numbers of the fractions that (a) first contain a detectable trace of copper; (b) contain the most copper, as estimated by eye; (c) correspond to the removal of the bulk of the copper from the column [e.g. the first fraction after (b) in which no blue tint can be discerned]; and (d) the first fraction in which copper cannot be detected by the usual qualitative tests. A big gap between fractions (c) and (d) indicates a marked 'tailing' of copper from the column. This may be reduced by the use of a lower flow rate or by the use of a finer mesh resin (e.g. 100–200 mesh, if available). It is impossible, however, to reduce the tailing beyond certain limits and there is little point in adopting a lower rate of flow unless a significant reduction in the tailing is achieved thereby.

Once the behaviour of copper under specified conditions has been established, repeat the experiment under the same conditions, but after loading the column with 10 or 15 ml. of M/10 ferric chloride solution (15 ml. of iron solution would correspond approximately in terms of milliequivs. of metal to 25 ml. of copper solution and the FeCl_3 solution should have a pH value of *ca.* 1). Record the numbers of the fractions that (e) first contain a detectable trace of iron; (f) contain most iron; (g) correspond to the removal of the bulk of the iron from the column; and (h) the first fraction, after (f),

EXPERIMENTS

in which iron cannot be detected by the usual qualitative tests.

A comparison of the two sets of results will show that copper is displaced more readily down the column than iron. Hence (a) should correspond to a lower fraction number than (e) and (b) to a lower fraction number than (f) and some degree of separation of copper from iron, if present together (e.g. using 15 ml. M/10 CuSO_4 and 10 ml. M/10 FeCl_3) is possible. To obtain a complete separation of copper from iron, however, (d) should correspond to a fraction number lower than that of (e) which is unlikely under the conditions suggested.

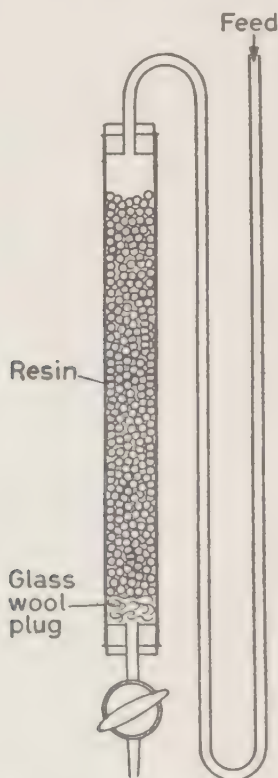


Figure 33. Non-draining column

A separation of copper from iron (III) might be achieved by the use of a longer column of approximately the same diameter. For this purpose a burette, with a glass wool plug just above the tap to support the resin bed, may be found useful. If the arrangement indicated in Figure 33 is adopted it is possible to dispense with the side arm at the outlet end

of the column. In this way the turbulent mixing, which may occur when a band of lower density liquid moves up the side arm behind one of higher density, may be avoided and the fractions are more sharply defined. At the same time a change from 50–100 mesh resin of normal cross-linking to one of either 50–100 or 100–200 mesh with 4 or 8 per cent cross-linking agent may be made.

As an extension to this experiment the separation of copper and iron (III) with phosphoric acid eluant of pH 0.5 might be tried. It will be found that with this eluant not only is the separation more readily achieved, but that iron (III) is displaced down the column more readily than copper¹. As will be explained later, this reversal of the order of elution is due to the fact that the eluant forms a complex selectively with the Fe^{3+} ions.

Conclusions

The separation or partial separation of copper from iron (III) with a hydrochloric acid eluant is an example of what might be termed straight elution chromatography. There is comparatively little tendency for the eluant to form strong complexes with either of the ions being separated and the order of elution is related directly to the order of relative affinities of the ions for the resin—the ion having the lower relative affinity for the resin is eluted first. This type of elution is applicable to the separation of alkali metal ions and, in the field of anion-exchange chromatography, to the separation of halide ions². It is not suitable, however, for the separation of ions of very similar chemical character such as those of the lanthanons. To separate these ions it is necessary to use a complexing eluant.

In complexing elution the eluant contains an anion which forms complexes with one or more (generally all) of the ions to be separated. One result of the complex formation is to cause an effective reduction in the number of metal ions present in solution, which in itself tends to increase the efficiency of separation³. A second, and probably more important, factor is that the stabilities of the complexes formed by the various cations with the complexing agent will differ. If, as happens

EXPERIMENTS

with the lanthanons, the most stable complex is formed with the ion most readily eluted, this ion tends to remain in the aqueous phase and not to be resorbed so readily by the resin; hence the passage of the ion in the leading band down the column is speeded up. Under the same conditions the ion in the final band, which will form the least stable complex, will not be so readily displaced down the column by the effect of complex formation. It will also tend to be retarded by its own greater relative affinity for the resin. The two effects are complementary and together enhance the degree of separation achieved³.

The iron (III)–copper separation with a phosphoric acid eluant is abnormal in that the complex formation does not reinforce the original separation, but actually reverses it. The complex formation between iron (III) and phosphate is very marked whereas that between copper and phosphate is negligible. Hence the iron tends to remain in solution as a complex ion whilst the copper ions are resorbed at each stage on passing down the column. The complexing eluant is a selective one in this case. Such behaviour is less common than that typified by the lanthanon separation.

The successes of ion-exchange chromatography have been mainly in the separation of very similar ions such as the lanthanons, the heavier actinons, or the zirconium–hafnium or niobium–tantalum pairs, the separation of elements of the same periodic sub-group (e.g. the alkali metals or the halide ions), or the separation of amino acids. Separations of dissimilar elements such as copper (II) and iron (III), which served nevertheless as a simple and convenient example for Experiment 12, are not as useful since they can generally be achieved more readily by conventional chemical methods.

Finally, it cannot be stressed too strongly that extreme care and patience provide the key to success in chromatographic separations.

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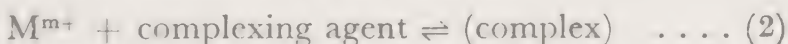
Chapter 11

ION EXCHANGE IN THE STUDY OF COMPLEXES

It is evident from the use of complexing eluants in ion-exchange chromatography, discussed in the previous chapter, that complex formation leads to a displacement of ion-exchange equilibria. Thus the reaction:



will be displaced to the right by the reduction in the concentration of free cations caused by the reaction:



Hence the formation of complexes may be detected by comparing the position of the ion-exchange equilibrium [equation (1)] in both the absence and the presence of a suspected complexing agent, but otherwise under identical conditions. A displacement of equilibrium of equation (1) to the right in the second case will indicate complex formation. For this purpose it does not matter from which side the equilibrium is approached. It is possible to use hydrogen form resin and to introduce the metal into the system as a solution of one of its salts or to use the resin in the metal ion form and to introduce the hydrogen ions in the form of a solution of an acid. In some cases, e.g. study of complex formation in neutral or alkaline media, it may be preferable to study the exchange of metal ions with sodium or ammonium ions rather than with hydrogen ions, but this in no way affects the principles involved.

Under suitable conditions, i.e. low metal ion concentration in the system (to enable concentration terms to be substituted for activities in the appropriate stage of the calculation) it is possible to deduce the formation constant of the

EXPERIMENTS

complex from the experimental data (or the formation constants if several stages of complex formation occur). An elegant treatment along these lines has been given by Schubert and his co-workers^{1,2}.

If it is desired to assess the relative orders of complex formation between a cation and various ligands only, then it is sometimes convenient to use the metal form of the resin, as already suggested. Samples of the resin (say 0.5 g in the metal form) are allowed to come to equilibrium with a fixed volume (say 50 ml.) of solutions containing the various ligands, but otherwise identical (with respect to non-complexing ions present, pH, etc.). The amount of metal found in the solution at equilibrium is a measure of the extent to which the reaction of equation (1) has proceeded from left to right and will be greatest in the case where complex formation is most marked. Thus if various samples of resin in the form M^{m+} are allowed to come to equilibrium with solutions of perchloric, nitric and hydrochloric acids of, say, pH 0.5, the amount of metal passing into the aqueous phase in the case of perchloric acid, which is the least likely to form complexes with the cation, must correspond closely to the state of simple equilibrium according to equation (1) with a minimum of disturbance from complex formation [equation (2)]. It is likely that with the other acids, the amount of metal removed will exceed that found with perchloric acid and the greater the amount of metal removed above that value, the greater the complex formation.

Since the exchanging ion is hydrogen its concentration must be the same in each case and hence the comparison must be made with the same initial hydrogen ion concentration (or pH) in each case. For a series of solutions of various monobasic acids, solutions of the same pH, corresponding very nearly to the same hydrogen ion concentration, will contain approximately the same molar concentration of anions; hence the comparisons are made at comparable ligand concentrations. Many weak polybasic acids, such as phosphoric acid, behave as monobasic acids in acid solutions (even sulphuric acid tends to be monobasic at low pH) and hence may be included in the series. Although a solution of phosphoric acid of pH 0.5 is 2 M or more in phosphate this is mainly

present as un-ionized phosphoric acid and the concentration of dihydrogen phosphate ions therein will be comparable with the concentration of perchlorate ions in a perchloric acid solution of the same pH.

It is possible to derive information of a more quantitative character, however, from experiments in which the sorption of the metal ions by the exchanger is studied. Not only is it then possible to employ procedures similar to those of Schubert—mentioned on p. 126—but if the complex formed by the reaction of equation (2) is charged, its sorption by either a cation- or anion-exchanger (depending on the charge) is possible. Thus Kraus and his co-workers³⁻⁵ have made an extensive series of studies on the sorption of anionic complexes of metals by anion exchangers which have provided useful information concerning such complexes. Similarly, knowledge of ferric phosphate and similar complexes has been increased by the study of their sorption on both cation- and anion-exchange resins^{6,7}.

A review of the use of ion-exchange in the study of complexes has been given by Salmon⁸ and this, together with the other references given, should be consulted for further details. In this brief introduction to the subject, a disproportionate amount of the discussion has been devoted to the method employing the metal form of the resin. This is solely because it forms the basis of the principal experiment in this chapter which is designed so that the student can learn as much as possible from a comparatively simple experiment.

Experiment 13. Studies of Complex Formation by Use of the Metal Form of an Exchanger

Prepare 8–10 g of the copper form of a strongly acidic cation-exchange resin by a procedure of the type described in Experiment 5. To ensure complete conversion to the metal form, the copper sulphate solution should be passed through the column until the copper content of the effluent is the same as that of the inflowing solution. The column should then be washed with water until the washings are neutral in reaction in methyl orange. Connect the outlet of a wash bottle to the

EXPERIMENTS

outlet of the column by a rubber tube, invert the column over a Buchner funnel, and transfer the resin to the funnel by a flow of water from the wash bottle. Give the resin a further rinse and remove as much as possible of the water from the resin by suction. Transfer the resin to a basin, cover lightly with filter paper and leave it to dry for at least three days at a temperature of 25–30°C. A similar quantity of resin in the iron (III) form should be prepared in the same way by use of 0.1 M ferric chloride solution (this should be a clear solution at pH 1.0).

Weigh out a 0.5 g sample of each of the two air-dried resins just prepared and transfer them to small columns (10 cm × 1 cm) according to the method of Experiment 3(a). Displace the copper from the resin by use of 2 N nitric acid and the iron by use of 2 N hydrochloric acid according to the procedure of Experiment 4(a) but collect the eluates in 250 ml. graduated flasks. Use 150 ml. acid only and follow this with water to a total volume of 250 ml. Calculate the iron or copper present in an aliquot of the eluate, wash the resin in each column thoroughly with water and determine its hydrogen ion capacity by the method of Experiment 3(c). Calculate the percentage of the capacity of each form [Cu(II) or Fe(III)] of the resin actually in the metal form. At least 90 per cent of the capacity should be taken up by the metal for the resin to be used in the experiments which follow.

Prepare stock solutions of nitric, hydrochloric and phosphoric acids all having a pH of 0.5 (if a pH meter is not available use 0.3 N HNO_3 , 0.3 N HCl , and 1.90 M H_3PO_4 solutions respectively).

Transfer two 50 ml. portions of each of these three stock solutions to dry 150 ml. conical flasks and add to each of one set of three 0.5 g portions of copper form resin and to each of the other set 0.5 g of iron form resin. Stopper each of the six flasks firmly with a clean rubber bung and leave to stand for one week with occasional gentle swirling of the contents (make certain that all the resin is wetted by the solution). Remove 25 ml. of the liquid phase with a pipette taking care not to draw up any resin beads (if this proves difficult, filter through a dry Whatman No. 1 paper in a dry

funnel into a dry beaker and take 25 ml. of the filtrate) and determine the copper or iron present in each aliquot. Calculate the percentage of metal that has been removed from the resin phase in each case (it may be assumed that so little water is sorbed by the air-dried resin from the solution that the 25 ml. portion withdrawn for analysis does, in fact, represent exactly half the aqueous volume at equilibrium).

Assuming that nitric acid shows little or no tendency to form complexes with either of the metal ions at pH 0.5, assess the relative tendencies of the other two acids to form complexes with each metal. The marked tendency for iron (III) to form phosphate complexes, which was mentioned in the previous chapter should now be readily apparent. These experiments may be extended by the use of solutions of other pH values and of other acids (including perchloric acid, if possible).

Experiment 14. Preliminary Studies in the Sorption of Complex Ions

To each of five dry 150 ml. conical flasks, add 30 ml. of a ferric chloride solution (0.1 M, pH 1.25). To the first flask then add 20 ml. of water; to the second, 15 ml. of water and 5 ml. 0.3 M phosphoric acid; to the third, 10 ml. of water and 10 ml. 0.3 M phosphoric acid; to the fourth, 5 ml. of water and 15 ml. 0.3 M phosphoric acid; to the fifth, 20 ml. of the phosphoric acid solution (either burettes or pipettes may be convenient for making these additions). Introduce 0.5 g strongly acid cation exchanger (50–100 mesh) into each flask, stopper it firmly with a rubber bung and leave for a week, swirling the contents from time to time.

After the period of standing, filter the contents of each flask through a small column into a dry filter flask using suction, according to the method of Experiment 2(b) (see *Figure 26*). Change the filter flask before transferring any resin remaining in the flask to the column, however, so that the filtrate may be kept for analysis. Maintain the suction applied to filter flask as high as possible, both when effecting the transfer (by a jet of water) of the resin, adhering to the flask walls, to the column, and also when washing the resin

EXPERIMENTS

with water afterwards. In this way any of the original solution adhering to the resin is rapidly washed away. If it were left in a partly diluted form in contact with the resin, the exchanger would tend to come to equilibrium with this new solution; hence a rapid initial washing of the resin is essential.

Fit the column with a side tube (*Figure 27*) and fill it with water as described in Experiment 2(b) and continue the washing with a downward flow of water until the washings are neutral to methyl orange. Displace the species sorbed on the resin with 2 N nitric acid, as described for the elution of copper in Experiment 4(a), and collect the eluate and washings in a 500 ml. graduated flask. Use aliquot samples for the determination of iron (between $\frac{1}{2}$ and $1\frac{1}{2}$ mg atoms present in total eluate from 0.5 g resin) and phosphate (up to $\frac{3}{4}$ mg moles of PO_4 may be present when the resin has been in contact with solutions containing the higher proportion of phosphate⁷. Calculate the mg moles (or mg atoms) of each sorbed per equivalent of resin; since the resin is in the hydrogen form after the elution, its capacity may be determined, after washing, by the method of Experiment 3(a). For a fuller method of treatment of the results, the paper of Holroyd and Salmon⁹ may be consulted, but a casual inspection will show that a cationic complex containing phosphate groups is sorbed under the prescribed conditions.

Conclusions

The results of Experiment 13 should help towards an understanding of the observations made in Experiment 12. Studies of complex ions made by ion-exchange methods may in fact result in developments in chromatography with new complexing eluants. Where qualitative indications as to extent of complex formation only are required, Experiment 13 may provide a useful pattern for a programme of study. Otherwise Experiment 14 or even more complex experimental procedures will have to be used as the basis of study.

The ion-exchange methods of studying complex ions present in solution have provided a valuable and much needed additional technique at the service of those investigating complex

systems. It is hoped that the brief introduction to the field given in this chapter may have the effect of inducing the reader to look further into this interesting field for himself.

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INDEX

- Absorption,
 - of non-electrolytes, 34
 - of organic ions, 35
- Acid exchange,
 - with strongly basic resins, 9
 - with weakly basic resins, 10
- Acids, preparation of, 110
- Affinity, 37, 82, 96
 - coefficient, 37
 - relative, 37
 - stoichiometric, 37
 - order of,
 - with univalent anions, 41
 - with univalent cations, 39
- Aluminosilicates, 2
 - in water treatment, 2, 3
- Anion exchanger,
 - capacity of, 6
 - by batch method, 79
 - by column method, 86
 - for chloride and sulphate ions, 89
 - strong base and total, 85
 - chloride form, 78, 86
 - conversion from one form to another, 87
 - equivalence of exchange with, 89
 - hydroxide form, treatment of, 78
 - preparation of air-dried chloride form, 78
 - regeneration of, 12, 95
 - strongly basic,
 - presence of weak base sites in, 85
 - use in demineralization, 117
 - use of carbonate form in place of hydroxide in demineralization, 117
 - titration curve, 8
 - weakly basic, use in demineralization, 117
- Base exchange, 1
 - with aluminosilicates, 2
 - with soils, 1
- Base exchange—*continued*
 - with strongly acidic resins, 8
 - with weakly acidic resins, 9
- Bases, preparation of, 110
- Break-through, 52
 - capacity, 53, 92
 - curve, shape of, 94
 - in relation to relative affinities, 96
 - of ions in column operation, 91
 - volume, 53
- Capacity,
 - of a resin,
 - by batch method, 79
 - by column method, 85
 - of air-dried resins, 84
- Carboxylic resins, equivalent materials, 27
- Catalysis, 11
- Cation-exchange equilibria, 37
- Cation exchanger,
 - capacity of, 6
 - by batch method, 79
 - by column method, 85
 - for hydrogen, silver and cupric ions, 88
 - conversion from one form to another, 86
 - equivalence of exchange with, 87
 - occurrence and elimination of reducing properties in, 105
 - preparation of air-dried hydrogen form, 75
 - regeneration of, 12, 94
 - titration curve, 7
- 'Channelling' in columns, 53, 67, 119
- Chelating resins, 26
- Chloromethylation, 22
 - of cross-linked polystyrene, 24
- Chromatographic grade resins, 28
- Chromatography, 50, 119
- Colloidal substances, effect of, in ion exchange, 105
- Column,
 - behaviour of resins, 5

- Column**—*continued*
 efficiency in relation to relative affinities, 96
 even packing of resin bed in, 92
 filling with water by upward flow, 81
 operation,
 analysis of effluent, 70
 flow rates used in, 90
 use of burette as, 122
- Columns,**
 behaviour of, 50
 construction of, 66, 67
- Commercial ion-exchange resins, 29**
- Complex ion formation,**
 detection of by ion exchange, 125
 effect of,
 on elution order in chromatography, 123
 on sorption of ions, 96, 105
 quantitative studies, 127
 use of metal form resin in studies of, 127
- Complex ions,**
 formation constants, from ion-exchange data, 125, 126
 preliminary studies in sorption of, 129
- Cross-linked polystyrene, 14**
 chloromethylation of, 22, 24
 laboratory preparation, 17
 preparation of, 15
 sulphonation of, 14, 18
 swelling of, 17, 18
- Cross-linking, effect on swelling, 18**
- De-ionization, 11**
- Demineralization, 44**
 of water, 112
 three-column system, 116
 two-stage, 115
 use of mixed bed resin in, 115
- Displacement development, 58**
- Divinylbenzene, 15–17**
 copolymerization of, 15
- Donnan membrane equilibrium, 33**
- Effluent, analysis of, 70**
- Electrolyte penetration, 33**
- Elution, 59, 70**
 chromatography, 120
 curves, 54
- Elution**—*continued*
 gradient, 63
 theory of, 60
 with complexing agents, 63, 71, 123
- Equivalent ion-exchange resins, 27**
- Exchange,**
 capacity, 6
 of anion-exchange resin, 6
 of cation-exchange resin, 6
 equivalence of, 87
 rate of, 82, 90
 reversible nature of, 90
 time to be allowed for, 87
- Film diffusion, 46**
 as rate-determining process, 47, 84
- Fine mesh resins, 29**
- Flow rates,**
 in analytical uses, 100
 in ion-exchange chromatography, 119
- Fraction cutters, 69**
- Frontal analysis, 56**
- Gradient elution, 63**
 apparatus for, 67
- Hydrolyzable substances, procedure for the analysis of, 105**
- Inorganic ions, separation of, 71**
- Insoluble substances,**
 analysis of, 102
 principles involved in, 106
- Ion exchange, analytical uses of, requirements for, 99, 100**
- Ion-exchange,**
 apparatus, 65
 chromatography, 11, 50, 56, 119
 abnormal elution order arising from selective complexing, 124
 applications of, 124
 elution order, 123
 preliminary studies in, 120
 requirements for, 119
 results of complex formation in, 123
 straight elution, 123
 use of complexing eluant, 63, 71, 123

- Ion-exchange**—*continued*
 column,
 capacity of, 53
 columns,
 behaviour of, 50
 equilibria, 34
 disturbed by complex formation, 125
 uni-bivalent, 41
 uni-tervalent, 43
 kinetics, 44
 papers, 26
 resins,
 air bubbles trapped between beads, 78, 85
 analytical grade, 78
 as catalysts, 11, 13
 capacity of, 6
 column behaviour, 5
 commercial, 27–9
 discovery, 3
 equivalent, 27
 for chromatography, 28
 cross-linking of, 30, 120
 particle size of, 30, 119
 for laboratory use, 30
 fracture of, under drastic treatment, 78
 of low degree of cross-linking, marked swelling of, 78
 preliminary treatment of, 75
 preparation of, 14
 properties of, 7, 31
 stability of, to chemical attack, 105
 styrene based, 3, 14
 swelling of, 31, 78
 transfer of, to column, 81
 transfer of, to flask, 84
 weighing out, 84
 techniques, 65
Ion-exclusion, 26
Ions,
 affinities of, 5
 amphoteric, separation of, 71
 complete sorption of, 90
 interfering, removal of (in analytical chemistry), 103
Kinetics, of ion exchange, 44
Membrane equilibrium, 33
Methacrylic acid, copolymerization of, 21
Migration of ions in resins, impeded by contraction of beads in strong electrolytes, 97
Mixed resin,
 filling column with, 115
 use in demineralization, 115
Nernst diffusion layer, 46
Neutralization,
 of acids,
 with strongly basic resins, 9
 with weakly basic resins, 10
 of bases,
 with strongly acidic resins, 8
 with weakly acidic resins, 9
Non-electrolytes, absorption of, 34
Organic ions,
 absorption of, 35
 separation of, 71
Particle diffusion, 46
 as rate-determining process, 47, 84
Plate theory, 60
Preparative chemistry, use of ion exchange in, 109
Purification processes, use of ion exchange in, 109
Rate-controlling processes, 45
Recovery processes, use of ion exchange in, 110
Regenerant solutions, strength of, 97
Regeneration, 2
 accompanied by chemical change in ions desorbed, 98
 complete, 90, 91
 effect of acid strength in, 95
 removal of last traces of sorbed ions in, 97
 studies of, 94
Relative affinity coefficient, 37
Resin,
 beads, removal of air bubbles, 85
 bed,
 even packing of, 92
 washing by upward flow of water, 75
Salt-splitting, 5

- Salt-splitting—*continued*
 - with strongly acidic resins, 8
 - with strongly basic resins, 9
 - with weakly acidic resins, 9
 - with weakly basic resins, 10
- Salts, preparation of one from another, 111
- Self-sharpening boundary, 54
- Separation factor, 62
- Separation of ions,
 - achieved by changes in oxidation or co-ordination states, 106
 - by ion-exchange chromatography, 50, 119
 - chromatographic procedure, 123
 - conditions required for, 107
- Simple exchange applications, 11
- Soluble salts, analysis of, 104
- Stoichiometric relative affinity coefficient, 37
- Strongly,
 - acidic resins, 4
 - base exchange with, 8
 - characteristics of, 12
 - neutralization of bases with, 8
 - order of affinity with, 39, 43
 - preparation of, 18
 - salt-splitting with, 8
 - structure of, 4
- basic resins, 4
 - acid exchange with, 9
 - behaviour of,
 - type I, 35
 - type II, 35
 - characteristics of, 12
 - equivalent materials,
 - type I, 27
 - type II, 27
 - exchange capacity of, 24
 - laboratory preparation of, 22
 - neutralization of acids with, 9
 - order of affinity with,
 - type I, 41
 - type II, 41
 - preparation of, 21
 - type I, 22
 - type II, 22
 - salt-splitting with, 9
 - stability of,
 - type I, 24
 - type II, 24
 - structure of, 4
- Sulphonated,
 - coal, 3
 - phenolic resins, equivalent materials, 27
 - polystyrene resins,
 - equivalent materials, 27
 - ion-exchange capacities, 21
 - preparation of, 18
- Sulphonation,
 - of cross-linked polystyrene, 14, 18
- Suspension polymerization, 15
- Swelling of ion-exchange resins, 31, 78
- 'Tailing',
 - in chromatography, 63, 121
 - in regeneration, 95
- Theoretical plate, 61
- Titration curves, 7
- Total salt concentration,
 - conditions required for determination of, 105
 - determination of, 100
 - effect of free acid or base in determination of, 104
- Water,
 - demineralization of, 112
 - demineralized, quality of, 116
- Water-regain, 24
- Water-softening, 2
 - with ion-exchange resins, 44
- Weakly,
 - acidic resins, 4
 - base exchange with, 9
 - characteristics of, 12
 - exchange capacity of, 21
 - neutralization of bases with, 9
 - preparation of, 21
 - salt-splitting with, 9
 - structure of, 4
 - basic resins, 4
 - acid exchange with, 10
 - characteristics of, 12
 - exchange capacity of, 25
 - neutralization of acids with, 10
 - preparation of, 24
 - salt-splitting with, 10
 - structure of, 4
- Zeolites, 2

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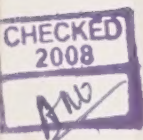
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